

The Systematic Identification of
ORGANIC COMPOUNDS

BY RALPH L. SHRINER AND REYNOLD C. FUSON

THE SYSTEMATIC IDENTIFICATION OF ORGANIC COMPOUNDS

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The Systematic Identification of
ORGANIC COMPOUNDS
A LABORATORY MANUAL

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THIRD EDITION

1948

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PREFACE TO THE THIRD EDITION

In this edition increased recognition is given to the fact that the primary feature of the student's assignment and the wellspring of his interest is the identification of unknown compounds. He is no longer directed to perform numerous practice experiments on solubility and in the use of classification reagents but is advised to carry out such control and practice experiments as are needed, in view of his previous training. However, the practice experiments on solubility determinations, elementary analyses, and classification tests are retained for the benefit of students for whom they may be necessary.

Chapter II contains a complete outline of the experimental work to be performed by the student. Each of the remaining chapters corresponds to a step in the identification process.

Chapter VI, as well as many other sections of the book, has been entirely rewritten, chiefly in the interest of increased clarity. A number of additional classification reagents are introduced, and additional procedures for the preparation of derivatives are given.

Many changes have been made in the values of the physical constants listed in the tables, but the original plan of these tables has been retained.

One of the difficulties encountered in the use of the previous edition was the location of a given compound in the tables by reference to the index. This difficulty has been eliminated by including the melting points (of solids) and boiling points (of liquids) in the index itself. The page number indicates the page on which the compound is listed, and the melting or boiling point enables one to locate the entry with the minimum of difficulty.

The authors wish to thank the numerous students and teachers who have called attention to errors and suggested improvements. Especial thanks are due to E. C. Horning, Marvin Carmack, Douglas Bowen, C. C. Price, and H. R. Snyder for new and improved tests and procedures.

R. L. S.

R. C. F.

PREFACE TO THE FIRST EDITION

Laboratory courses designed to teach methods of identification of organic compounds have become increasingly popular during the past twenty-five years. Since the foundations in this field were laid by Mulliken, whose classic work, *The Identification of Pure Organic Compounds*, was published in 1904, several other excellent treatises of the subject have appeared, and the teaching of systematic identification has become widespread.

The importance of this type of course in the training of the chemist is now universally recognized. The ability to identify compounds—valuable as it is to organic chemists—is, however, not the primary reason for the great popularity of laboratory courses in the subject. The great difference between this and other types of laboratory courses usually included in chemical curricula is that as yet no scheme has been devised which reduces this work to the mere following of directions. At every step in the identification of compounds by present methods the student is required to exercise his own judgment. The student's faculty for careful observation, his ability to make correct deductions from his observations, and his originality in planning his work are at a premium in this type of course. From this point of view it is obvious that this sort of training is the best kind of experience for those preparing for research. In this work students not only become aware of the necessity for research but also are introduced to the methods which it involves.

A natural and important outgrowth of this interest in identification methods is the large amount of research which has been done recently in this field, particularly in connection with the preparation of derivatives suitable for characterization and identification work. A consequence of this is that the subject matter of these courses is in constant need of revision.

The present book is the outgrowth of several years of experience with the subject both on the pedagogical side and from the research point of view. Interest in this work at the University of Illinois was initiated by Professor C. G. Derick, who first gave a

course of this sort in 1908. The course was subsequently developed by Professor Oliver Kamm, whose excellent textbook on the subject appeared in 1922. The laboratory exercises herein presented are those used at the present time at the University of Illinois in a one-semester course of two three-hour laboratory periods a week. The work is of such nature, however, that it can be readily adapted to longer or shorter terms by merely increasing or decreasing the number of unknown compounds assigned for identification. The course is designed for students who have had a year of organic chemistry.

In the preparation of the book, use has been made of many methods to be found in works of a similar nature. Chief among these are Mulliken's *The Identification of Pure Organic Compounds*, Kamm's *Qualitative Organic Analysis*, Clarke's *Handbook of Organic Analysis*, Staudinger's *Introduction to Qualitative Organic Analysis*, Porter, Stewart, and Branch's *Methods of Organic Chemistry*, and Bargellini's *Esercizi numerici di chimica organica*. To the authors of these, grateful acknowledgment is hereby made. For many of the innovations contained in this book the authors are indebted to other teachers of the subject here and elsewhere. Throughout the preparation of the manuscript Professor C. S. Marvel has rendered constant and invaluable assistance. Professors John R. Johnson, A. W. Ingersoll, S. M. McElvain, G. H. Coleman, Wallace R. Brode, Ralph Connor, and C. F. H. Allen have all contributed helpful suggestions which the authors gladly acknowledge. Finally, to the hundreds of students who have used these directions at the University of Illinois and who have been the final judges of the worth of the new features which appear in this book—to these, a special acknowledgment is made for indispensable assistance.

R. L. S.
R. C. F.

URBANA, ILLINOIS
September, 1935

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CHAPTER I

INTRODUCTION

The problem that is set for the student in this text is the identification of a number of compounds which are given to him as "unknowns." Most of these compounds are common substances, and all are described in the literature. Moreover, to afford the widest possible experience, the unknowns assigned to a given student ordinarily comprise a variety of types of compounds.

Certain of the unknowns, generally described as "simple" unknowns, are received by the student in relatively pure condition; others are met as components of mixtures. In either case the student will be expected to make certain that a given compound is pure before he proceeds with the identification. As a criterion of purity he will choose one or more physical constants, usually the melting point if the substance is a solid and the boiling point if it is a liquid. The determination of such constants is in any event a necessary part of the identification. If an unknown is found to be contaminated it should be purified before these constants are made a part of the record.

A systematic examination of the unknown is now undertaken. Experience has shown that, in general, the most valuable clues to the identity of a compound are the physical properties (including physical state, color, odor, and behavior on ignition). It is necessary, of course, to know what elements are present; these are detected by subjecting the compound to qualitative analysis.

From this point it is possible to proceed in various ways to accumulate information which will permit identification of the compound. In this book use is made of what is called the solubility class of the compound.

When the solubility class has been ascertained there frequently are definite indications as to which functional group or groups are in the molecule. Generally it is expedient to test for these groups by means of suitable reagents. These tests must be selected

in such a way as not merely to establish the presence of certain functional groups but also to exclude others from consideration.

At this point, but usually not before, it is advantageous to consult the literature. The homologous series or class being known, it is possible by reference to the physical constants of the unknown to exclude from consideration all but a few compounds of the chemical series or class of which the unknown is a member. It is then necessary to study the descriptions given in the literature of the compounds remaining and to devise a scheme for determining which is the compound under examination. The usual procedure involves the preparation of one or more derivatives.

On the basis of the foregoing principles, a somewhat detailed procedure, which is described in the next chapter, has been developed for examining an unknown. It is believed that adherence to this procedure will nearly always lessen the amount of time required to complete the identification.

The time can be reduced further by the use of smaller amounts of materials and the semi-micro technic. By suitable modifications the directions may be adapted to such small-scale operations.¹

¹ Schneider, *Qualitative Organic Microanalysis*, John Wiley & Sons, New York, 1946; Cheronis and Entrikin, *Semimicro Qualitative Organic Analysis*, Thomas Y. Crowell Co., New York, 1947.

CHAPTER II

THE IDENTIFICATION OF UNKNOWNNS

The following set of directions is intended as a guide to the student in the process of identifying an unknown. He will, of course, be expected to make a careful and systematic record of his observations; the preparation of such a record will be simplified greatly by the use of the suggested sequence of operations.

1. Preliminary Examination. Refer to Chapter III, pp. 17-18.

Note whether the substance is homogeneous, and record its physical state (solid or liquid), color, and odor. Perform the ignition test (p. 18), and record the results.

2. Physical Constants. Refer to Chapter IV, pp. 19-51.

If the unknown is a solid, determine the melting point (pp. 19-23). If the melting-point range is more than 2.0° , the compound should be recrystallized. If the unknown is a liquid or a very low-melting solid, determine its boiling point (pp. 24-32); the range of this constant should not exceed 5.0° except for very high-boiling compounds. Distillation is recommended if the boiling-point range indicates extensive contamination, if the compound is inhomogeneous, or if it appears to be discolored.

3. Analysis for the Elements. Refer to Chapter V, pp. 52-57.

Test the compound for the presence of nitrogen, sulfur, chlorine, bromine, and iodine (pp. 52-57). If a residue was noted in the ignition test, identify the metal which it contains.

Control Experiments. If the student is unfamiliar with the procedure for decomposing the compound or with the tests for the elements, he should carry out control experiments on a known compound at the same time that the unknown is tested. The compound to be used for the control experiment should, of course, contain nitrogen, sulfur, and a halogen.

4. Solubility Tests. Refer to Chapter VI, pp. 58-82.

Determine the solubility of the unknown in water, dilute hydrochloric acid, dilute sodium hydroxide, sodium bicarbonate solu-

tion, cold concentrated sulfuric acid, phosphoric acid, and ether (pp. 58-62). If the classification is doubtful, treat an accurately weighed sample with an accurately measured volume of solvent. If this measurement shows the substance to lie close to the borderline between two classes, the substance should be assigned to both classes.

Practice Experiments. Accurate deduction on the basis of the solubility tests requires practice on known compounds, and for this purpose an experiment (p. 61) has been provided.

When testing the solubility of the compound in water, the reaction of the solution or suspension to litmus and phenolphthalein should be determined.

When the solubility class (or classes) of the unknown has been determined, draw up a list of the chemical classes to which the compound may belong.

Preliminary Report. To avoid loss of time through mistaken observation, it is recommended that at this point the student submit to the instructor his data on the physical constants, elementary composition, and solubility behavior.

5. Classification Tests. Refer to Chapter VII, pp. 83-151.

From the evidence that has been accumulated deduce what functional group or groups are most likely to be present in the unknown, and test for them by means of suitable classification reagents. Thirty-six of the most common of these are mentioned in Chapter VII (p. 83), where directions for their use may be found. In the following list these tests are arranged according to the type of compounds for the detection of which they are suitable.

Unsaturation:

- (a) Potassium permanganate solution (p. 117).
- (b) Bromine in carbon tetrachloride (p. 93).

Halogens:

- (a) Alcoholic silver nitrate solution (p. 121).
- (b) Sodium iodide in acetone (p. 140).

Acids:

- (a) Duclaux constants (p. 146).
- (b) Neutralization equivalents (p. 128).
- (c) Distribution numbers (p. 147).

Alcohols:

- (a) The hydrochloric acid-zinc chloride reagent (p. 104).
- (b) Acid chlorides (p. 87).

- (c) Ceric nitrate (p. 96).
- (d) Iodic acid (p. 107).
- (e) Metallic sodium (p. 126).
- (f) Periodic acid (p. 115).

Amines:

- (a) Benzenesulfonyl chloride (p. 91).
- (b) Nitrous acid (p. 113).
- (c) Acid chlorides (p. 87).

Aldehydes:

- (a) Benedict's solution (p. 90).
- (b) Tollens' reagent (p. 145).
- (c) Fehling's solution (p. 98).
- (d) The fuchsin-aldehyde reagent (p. 101).
- (e) Sodium bisulfite solution (p. 127).

Aldehydes and Ketones:

- (a) Phenylhydrazine (p. 116).
- (b) 2,4-Dinitrophenylhydrazine (p. 97).
- (c) Sodium bisulfite solution (p. 127).
- (d) Sodium hypoiodite (p. 138).
- (e) Mercuric chloride-sodium ethoxide (p. 109).
- (f) Hydroxylamine hydrochloride (p. 106).

Aromatic Hydrocarbons:

- (a) Fuming sulfuric acid (p. 142).
- (b) Anhydrous aluminum chloride and azoxybenzene or chloroform (p. 88).

Ethers:

- (a) Hydriodic acid (p. 103).
- (b) Bromine water (p. 95).

Esters:

- (a) Sodium hydroxide solution (p. 129).
- (b) Saponification equivalent (p. 133).

Nitro Compounds:

- (a) Zinc and ammonium chloride (p. 149).
- (b) Ferrous hydroxide (p. 100).
- (c) Sodium hydroxide solution (p. 137).
- (d) Tin and hydrochloric acid (p. 144).

Phenols:

- (a) Bromine water (p. 95).
- (b) Ferric chloride solution (p. 98).
- (c) Acid chlorides (p. 87).

Indicate the reagents applied in the classification tests, the results, and the inference from each. Record any observations in

regard to the nature of the products formed in these tests which may be of use later in excluding compounds from the list of possibilities; e.g., if hydrolysis of a neutral nitrogen compound by acid yields no water-insoluble product, the substance cannot be a derivative of a water-insoluble acid. Neutralization (p. 128) and saponification (p. 133) equivalents may be recorded here also.

Control Tests. Unless the student has had previous experience with a given classification test, he should carry out a control test on a known compound at the same time that the test is applied to the unknown.

6. The Examination of the Literature. By reference to the literature prepare a list of compounds which boil or melt within 5° of the value observed for the unknown and which have the same elementary composition, the same solubility, and the same behavior toward the classification reagents as the unknown. Many of these are to be found in the tables in Chapter IX. However, it frequently is necessary to consult other sources. The following are recommended.

1. Clarke, *Handbook of Organic Analysis*.
2. Huntress and Mulliken, *Identification of Pure Organic Compounds*.
3. Kempf-Kutter, *Schmelzpunktstabellen*.
4. Richter, *Lexicon der Kohlenstoff Verbindungen*.
5. Beilstein, *Handbuch der organischen Chemie*.
6. Stelzner, *Literatur-Register der organischen Chemie*.
7. Meyer, Hans, *Nachweis und Bestimmung organischer Verbindungen*, 1933.
8. Meyer, Hans, *Analyse und Konstitutions-Ermittlung organischer Verbindungen*, 1931.
9. Rosenthaler, *Der Nachweis organischer Verbindungen*, 1914.
10. Heilbron, *Dictionary of Organic Compounds*, 1943.
11. *Chemical Abstracts*.

In deciding whether a compound actually possesses the physical constants observed, considerable latitude must be allowed for experimental error. Thus, if the boiling point is very high or the melting point very low, the range must be extended somewhat beyond 5° . Other constants such as specific gravity (p. 32), refractive index (p. 40), and neutralization equivalents (p. 128) (but not Duclaux (p. 146) constants) may be used, with proper allowance for experimental error, to exclude compounds from the list of possibilities. A complete list of possible compounds with derivatives for each should always be made even though a product

obtained in the classification tests appears to be a suitable derivative.

The systems of classification used in the above reference works vary considerably. In Clarke's *Handbook*, compounds are grouped according to homologous series, which are divided into solids and liquids arranged in the order of increasing values of the melting points and boiling points. The system used in Mulliken is unique and is described in detail on page 1. The tables of melting and boiling points have been arranged by Kempf and Kutter in the order of magnitude of these physical constants only, and without regard to solubility or class reactions. In the remaining references (4, 5, 6, 7, 8, 9, 10, 11) it is necessary to look up specific compounds according to molecular formula or name which the possibilities obtained from references 1, 2, and 3 may suggest.

At the same time that a list of possible compounds is being prepared, notes should be made concerning derivatives for the compounds. In this way much time may be saved. It is best to consult Chapter VIII on derivatives and note the types of compounds suitable for final identification. The same reference works cited above are used to obtain this information, and in addition the original literature references in Chapter VIII must be consulted.

7. The Preparation of Derivatives. Refer to Chapters VIII and IX, pp. 152 and 218.

The list of possible compounds which results from the preceding steps in the examination of an unknown usually contains compounds belonging to one or two types. The next step in the identification is the confirmation of the identity of one of these possibilities with the unknown and the simultaneous demonstration that each of the remaining possibilities differs in some way from the unknown. This final proof is accomplished by the preparation of a derivative. If the list of possibilities is long, it frequently is impossible to accomplish this unique characterization by means of a single derivative; further derivatives may then be necessary.

In eliminating compounds from the list of possibilities, one is not restricted to the use of derivatives. It is to be remembered that any sufficiently characteristic property such as specific gravity, refractive index, optical rotation, or neutralization equivalent may be employed.

The Properties of a Satisfactory Derivative. (a) A satisfactory derivative should be easily and quickly made and readily purified. This generally means that the derivative must be a solid, because, in the isolation and purification of small amounts of material, solids afford greater ease of manipulation, and melting points are more accurately and more easily determined than boiling points. The most suitable derivatives melt above 50° but below 250° . Most compounds that melt below 50° are difficult to crystallize, and a melting point above 250° is undesirable on account of possible decomposition and because the stem correction of the thermometer often amounts to several degrees.

(b) The derivative must be prepared by a reaction that produces a compound in good yield. Processes accompanied by rearrangements and side reactions are to be avoided.

(c) The derivative should possess properties distinctly different from those of the original compound. Generally, this means there should be a marked difference between its melting point and that of the parent substance.

(d) The derivative chosen should be one that will single out uniquely one compound from among all the possibilities. Hence the melting points of the derivatives to be compared should differ from each other by at least 5° .

Consult Chapters VIII and IX, and select a suitable derivative from those suggested. It will be noted that derivatives that are satisfactory for purposes of identification are numerous but often of limited scope. A few of the most useful are listed below; these should receive first attention when a derivative is sought.

Acids:

- (a) Amides and anilides.
- (b) *p*-Nitrobenzyl and *p*-bromophenacyl esters.

It is to be noted that Duclaux constants, partition coefficients, and the neutralization equivalents are very useful in this type of work and may take the place of a derivative. However, it seldom is advisable to depend upon them alone.

Alcohols:

- (a) Phenyl- and α -naphthylurethans.
- (b) 3,5-Dinitrobenzoates.

Aldehydes and Ketones:

- (a) Phenylhydrazones.
- (b) 2,4-Dinitrophenylhydrazones.
- (c) Semicarbazones.
- (d) Oximes.

Acid Anhydrides:

- (a) Acids.
- (b) Amides.
- (c) Anilides.

Acid Chlorides:

- (a) Acids.
- (b) Amides.
- (c) Anilides.

Alkyl and Aryl Halides:

- (a) Anilides.
- (b) Alkylmercuric halides.

Amines (Primary and Secondary):

- (a) Benzenesulfonamides.
- (b) *p*-Toluenesulfonamides.
- (c) Acetamides.
- (d) Benzamides.
- (e) Phenylthioureas.

Amines (Tertiary):

Addition compounds with

- (a) Chloroplatinic acid.
- (b) Methyl *p*-toluenesulfonate.
- (c) Methyl iodide.
- (d) Picric acid.

Aromatic Hydrocarbons:

- (a) Nitro derivatives.
- (b) Arylbenzoic acids.

Ethers (Aromatic):

- (a) Nitro derivatives.
- (b) Bromo derivatives.

Phenols:

- (a) α -Naphthylurethans.
- (b) Bromo derivatives.
- (c) Acetates.
- (d) Benzoates.

Many types of compounds can be hydrolyzed to acids, amines, alcohols, etc., and often are most easily identified by reference to

such products. In this group are acetals, acid anhydrides, acid chlorides, amides, esters, certain ethers, and nitriles.

Nitro, nitroso, azo, and hydrazo compounds can be reduced to the corresponding amines, and many compounds may be identified readily by reference to such reduction products.

The next step in the identification is the preparation of the derivative. Procedures for many of these are to be found in Chapter VIII. If other derivatives are made, the directions should be sought in the original literature. Richter, Stelzner, Beilstein, and *Chemical Abstracts* give references to original journal articles in which the procedures are described.

8. Mixtures. Refer to Chapter X, pp. 280-299.

When the simple unknowns have been identified, one or more mixtures will be assigned. It is understood that no mixture will contain more than five organic components. After obtaining the mixture from the instructor, proceed with the separation according to the methods outlined in Chapter VI. Many of the mixtures contain a volatile component which may be removed by heating the mixture on a steam bath. In dealing with a mixture of unknown composition, it is inadvisable to attempt distillation at higher temperatures.

When the components of the mixture have been separated, identify each according to the procedure followed for simple unknowns.

Mixed Melting Points. In identifying organic compounds, mixed melting points are very important and are used frequently. Instances have been observed, however, in which the mixing of two substances produces no depression in melting point. Hence the fact that two substances have the same melting point separately and when mixed is not sufficient to establish their identity. Moreover, it frequently happens that an authentic specimen of the compound is not available for a mixed melting point, and the student should be familiar with methods for identifying compounds without recourse to that device. Mixed melting points should, therefore, be offered as confirmatory evidence only in those rare instances where the system outlined above fails through lack of data.

9. Reports of Unknowns. After the identification of an unknown has been completed the results are reported on special

forms supplied by the instructor. The following specimen reports illustrate the correct procedure.

Specimen Reports on Unknowns

n-Butyl Alcohol
Unknown No. 1

Name John Smith
Date June 1, 1947

1. Physical Examination

(a) Physical State *liquid* (b) Color *none* (c) Odor *choking*
(d) Ignition Test *Burns with bluish flame—no residue.*

2. Physical Constants

(a) M. P. obs. ; Corr. (c) Sp. Gr. $0.812^{20^\circ}/4$
(b) B. P. obs. $114-117^\circ$; Corr. $115-118^\circ$ (d) n_D^{20} 1.3988

3. Elementary Analysis: F, Cl, Br, I, N, S, Metals *none*

4. Solubility Tests

H ₂ O	(C ₂ H ₅) ₂ O	NaOH	NaHCO ₃	HCl	H ₂ SO ₄	H ₃ PO ₄	Class
+	+						S ₁

Reaction to litmus *none* ; to phenolphthalein *none*

5. Classification Reagents

Reagent	Result	Inference
Acetyl chloride	Reaction—heat—fruity odor	Presence of OH group
Ceric nitrate	Red color	Presence of OH group
Br ₂ in CCl ₄	No unsaturation
2,4-Dinitrophenylhydrazine	No carbonyl group
Lucas reagent	Primary alcohol
Sodium hypiodite	No ppt.	No CH ₃ CHOH group

These tests indicate the presence of a primary alcohol group
Results of Special Tests (N.E., S.E., etc.)

6. Examination of the Literature

Possible Compounds	B. P.	Derivatives and Physical Constants			
		<i>3,5-Dinitrobenzoate</i>	<i>α-Naphthylurethan</i>	<i>Phenylurethan</i>	<i>Sp. gr.</i>
1. <i>n</i> -Butyl alcohol	117°	64°	71°	61°	0.810
2. <i>2</i> -Pentanol	119	61	76	..	0.810
3. <i>Methylisopropylcarbinol</i>	113	..	109	68	0.819
4. <i>Isobutyl alcohol</i>	103	86	104	86	0.805
5. <i>3</i> -Pentanol	116	97	71	49	0.820

7. Preparation of Derivatives

	1	2	3
Name	<i>3,5-Dinitrobenzoate</i>	<i>α-Naphthylurethan</i>	<i>Phenylurethan</i>
M. P. obs.	62-63°	63-69°	57-59°
M. P. in Lit.	64	71	61

8. Special comments

α-Picoline

Unknown No. 2

Name *John Smith*Date *June 1, 1947*

1. Physical Examination

(a) Physical State *liquid* (b) Color *light yellow* (c) Odor *like pyridine*
 (d) Ignition Test *Burns with luminous flame—no residue.*

2. Physical Constants

(a) M. P. obs. ; Corr. (c) Sp. Gr. $^{20}_4$ 0.945
 (b) B. P. obs. 126-130°; Corr. 127-131° (d) n_D^{20} 1.5025

3. Elementary Analysis: F, Cl, Br, I, S, Metals *None**N, Present.*

4. Solubility Tests

H ₂ O	(C ₂ H ₅) ₂ O	NaOH	NaHCO ₃	HCl	H ₂ SO ₄	H ₃ PO ₄	Class
+	+						S ₁

Reaction to litmus *basic* ; to phenolphthalein *basic*

5. Classification Reagents

Reagent	Result	Inference
<i>Acetyl chloride</i>	<i>No -OH, -NH₂, or -NHR</i>
<i>Hinsberg</i>	<i>NaOH: no ppt. only oil</i> <i>HCl: no ppt. clear soln.</i>	<i>Tertiary amine</i>
<i>2,4-Dinitrophenylhydrazine</i>	<i>No carbonyl group</i>
<i>Br₂ in CCl₄</i>	<i>No unsaturation</i>
<i>Nitrous acid</i>	<i>Green soln.</i>	<i>?</i>

These tests indicate the presence of *Tertiary amine*

Results of Special Tests (N.E., S.E., etc.)

6. Examination of the Literature

Possible Compounds	M. P. or B. P.	Derivatives and Physical Constants			
		<i>Methyl iodide</i>	<i>Picrate</i>		
1. <i>α-Picoline</i>	129°	230°	169°		
2. <i>Pyridine</i>	116	117	167		
3. <i>β-Dimethylaminoethyl alcohol</i>	153		96		
4.					
5.					

7. Preparation of Derivatives

	1	2	3
Name	<i>Picrate</i>	<i>Methyl iodide</i>	
M. P. obs.	<i>167-168°</i>	<i>225-228°</i>	
M. P. in Lit.	<i>169</i>	<i>230</i>	

8. Special Comments

*Isobutyric Acid*Name *John Smith*Unknown No. *3*Date *June 1, 1947*

1. Physical Examination

- (a) Physical State *liquid* (b) Color *colorless* (c) Odor *rancid*
 (d) Ignition Test *Burns with blue flame—no residue.*

2. Physical Constants

- (a) M. P. obs. ; Corr. (c) Sp. Gr. *0.948*
 (b) B. P. obs. *151-156°*; Corr. *152.5-157.5°* (d) n_D^{20} *1.3927*

3. Elementary Analysis: F, Cl, Br, I, N, S, Metals *None*

4. Solubility Tests

H ₂ O	(C ₂ H ₅) ₂ O	NaOH	NaHCO ₃	HCl	H ₂ SO ₄	H ₃ PO ₄	Class
+	+						<i>S₁</i>

Reaction to litmus *acidic* ; to phenolphthalein *none*

5. Classification Reagents

Reagent	Result	Inference
<i>2,4-Dinitrophenylhydrazine</i>	<i>No carbonyl group</i>
<i>Acetyl chloride</i>	<i>No -OH, NH₂, or -NHR</i>
<i>Br₂ in CCl₄</i>	<i>No unsaturation</i>
<i>Na</i>	<i>Vigorous reaction</i>	<i>Active hydrogen</i>

These tests indicate the presence of *an acid*

Results of Special Tests (N.E., S.E., etc.)

N.E. = 87 ± 1 ; *Duclaux numbers*: 24.9, 20.7, 16.0

6. Examination of the Literature

Possible Compounds	M. P. or B. P.	Derivatives and Physical Constants			
		<i>Anilide</i>	<i>p-Toluide</i>	<i>p-Bromo-phenacyl</i>	
1. <i>Isobutyric acid</i>	155°	105°	104°	77°	
2. <i>Propionic acid</i>	141	103	124	63	
3. <i>n-Butyric acid</i>	164	95	72	63	
4. <i>Pivalic acid</i>	164	129	120	76	
5.					

7. Preparation of Derivatives

	1	2	3
Name	<i>Anilide</i>	<i>p-Toluide</i>	<i>p-Bromophenacyl</i>
M. P. obs.	103-104°	103-104°	75-76°
M. P. in Lit.	105	104	76

8. Special Comments *Duclaux numbers indicate isobutyric acid.*

CHAPTER III

PRELIMINARY EXAMINATION

1. Physical State. A note is made as to whether the unknown substance is a liquid or solid. This information is useful in consulting tables of compounds (Chapter IX), which are subdivided on this basis.

2. Color. The color of the original sample is noted as well as any change in color which may occur during the determination of the boiling point (p. 24).

The color of some compounds is due to impurities; frequently these are produced by slow oxidation of the compound by oxygen in the air. Aniline, for example, usually is reddish brown, but a freshly distilled sample is nearly colorless.

Many liquids and solids are definitely colored because of the presence of chromophoric groups in the molecule. Many nitro compounds, quinones, azo compounds, carbonium salts (triphenylmethane dyes), and compounds with numerous conjugated systems are colored. If an unknown compound is a stable, colorless liquid or a white crystalline solid, this information is valuable because it excludes chromophoric functional groups as well as many groups which by oxidation would become chromophores.

3. Odor. Many types of organic compounds have characteristic odors. It is not possible to describe odors in a precise manner, but the student should become familiar with the odors of common compounds. Alcohols have odors different from those of esters; phenols from amines; aldehydes from ketones. Mercaptans, isonitriles, and pentamethylenediamine usually are described as possessing disagreeable odors—but they differ from each other. Moreover, the odor is most pronounced in the lower-molecular-weight members of a class since these are more volatile. Benzaldehyde, nitrobenzene, and benzonitrile all have the odor of bitter almond oil. Eugenol, coumarin, vanillin, methyl salicylate, and isoamyl acetate all have characteristic odors which are

easily remembered. Hydrocarbons also differ in their odors—toluene, hexane, isoprene, indene, pinene, and naphthalene possess distinctive odors.

The student should note *cautiously* the odors of the common organic compounds used in the tests and compare them with the odors of his own unknowns.

4. The Ignition Test. Procedure. A sample of 0.1 g. of the substance is placed in a porcelain crucible cover and brought to the edge of a flame to determine inflammability. It is then heated gently over a low flame and finally ignited strongly. A note is made of: (1) inflammability and nature of the flame (is the compound explosive?); (2) if the compound is a solid, whether the compound melted and the manner of its melting; (3) odor of gases or vapors evolved (caution); (4) residue left after ignition. Will it fuse? If a residue is left the lid is allowed to cool, a drop of distilled water is added, and the solution tested with litmus. A drop of dilute hydrochloric acid is added. Is a gas evolved? A flame test with a platinum wire is made on the hydrochloric acid solution to determine the metal present.

Try this test on: (1) ethanol; (2) toluene; (3) barium benzoate; (4) copper acetate; (5) sodium potassium tartrate (Rochelle salts); (6) sucrose.

Discussion. Many liquids burn with a characteristic flame that assists in determining the nature of the compound. If the substance is inflammable the usual precautions must be taken in subsequent manipulation of such compounds. This test also shows whether a melting point of a solid should be taken and indicates whether the solid is explosive.

If an inorganic residue is left after ignition it should be examined for the metallic elements. Since the number of metallic elements commonly found in organic compounds is not very large a few simple tests will usually determine the nature of the metal present. If the flame test indicates sodium, a sample of the compound should be ignited on a platinum foil instead of a porcelain crucible cover. Why?

Questions

1. If an inorganic residue is left on ignition, in what solubility class would you expect the compound to fall?
2. Name some residues that fuse on ignition. Name some that do not fuse.
3. Name some organometallic compounds that leave no residue on ignition.

CHAPTER IV

THE DETERMINATION OF PHYSICAL PROPERTIES

Melting Points

If the ignition test indicates that a solid unknown melts, its exact melting point is determined by one of the following procedures.

Procedure A. A thin-walled capillary tube about 1 mm. in diameter is made by heating a piece of 15-mm. glass tubing in a flame until the glass is soft and then drawing it out. The capillary portion is cut into lengths of about 6 cm., and the larger end of each tube is sealed in a flame. A small amount of the compound is powdered on a clay plate, and some of the powder is introduced into the capillary tube. The capillary tube is then held vertically and gently rubbed with a file, which causes the powder to settle to the bottom. The material is packed by tapping the tube on the desk; the tube is then fastened to the thermometer by means of a rubber band so that the sample is close to the mercury bulb (Fig. 1). Cottonseed oil is placed in the beaker, which is heated by a low flame. A cylindrical metal shield, open at top and bottom, is clamped in the position shown in Fig. 1 in order to protect the flame from drafts. The rate of heating should be such as to cause a rise in temperature of about 1° or 2° per minute, and the oil bath must be stirred continuously. The temperature at which

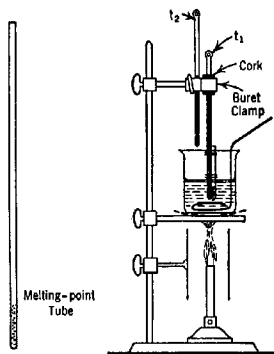


FIG. 1. Melting-point apparatus.

the compound starts to melt and that at which it is entirely liquid are noted. These values are recorded as the melting-point range. The temperature recorded by the auxiliary thermometer (t_2) is also noted; the bulb of this thermometer should be placed midway between the surface of the oil and the top of the mercury thread in t_1 . The stem correction is calculated by means of the formula:

$$\text{Correction} = +N(t_1 - t_2)0.000154$$

where N = degrees of mercury thread above the level of the oil bath; t_1 = observed melting point; t_2 = average temperature of mercury thread. This correction is added to the observed melting point. Both the observed and the corrected melting points should be recorded for an unknown compound.

It is often time-saving to run a preliminary melting-point determination raising the temperature of the bath very rapidly. After the approximate melting point is known, a second determination is carried out by raising the temperature rapidly until within 5° of the approximate value and then proceeding slowly as described above. A fresh sample of the compound should always be used for each determination.

Discussion. The thermometer should always be calibrated by observing the melting points of several pure compounds such as the following:

M. P. (cor.)		M. P. (cor.)	
0°	Ice	187°	Hippuric acid
53	<i>p</i> -Dichlorobenzene	200	Isatin
90	<i>m</i> -Dinitrobenzene	216	Anthracene
114	Acetanilide	238	Carbanilide
121	Benzoic acid	257	Oxanilide
132	Urea	286	Anthraquinone
157	Salicylic acid	332	<i>N,N</i> -Diacetylbenzidine

If care is taken to use the same apparatus and thermometer in all melting-point determinations, it is convenient and time-saving to prepare a calibration curve such as that shown in Fig. 2. The observed melting point of the standard compound is plotted against the corrected value, and a curve, OA , is drawn through these points. In subsequent determinations the observed value, B , is projected horizontally to the curve and then vertically down to give the corrected value, C .

It should be noted that such a calibration curve includes corrections for inaccuracies in the thermometer and stem correction.

It is important to record the melting-point range of an unknown compound since this is a valuable index of purity. A large majority of pure organic compounds melt within a range of 0.5° or melt with decomposition over a narrow range of temperature (about 1°).

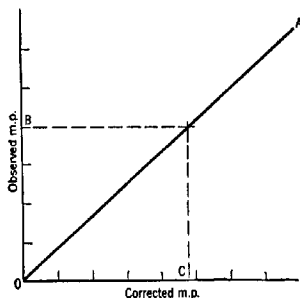


FIG. 2. Calibration curve.

If the melting-point range or decomposition range is wide, the compound should be recrystallized from a suitable solvent and the melting or decomposition point again determined. Many organic compounds such as amino acids, salts of acids or amines, and carbohydrates melt with decomposition over a considerable range of temperature.

Questions

1. Why should the rate of heating influence the melting point?
2. Why is the melting point of a sample which has once been melted often quite different from the original value?
3. What is a mixed melting point? What is the value of such a determination? Are there any exceptions which render the use of mixed melting points questionable?

Procedure B. If a compound melts above 250° its melting point may be determined by means of the Maquenne block. A diagrammatic sketch of a simple gas-heated block is shown in Fig. 3.

A special thermometer (A) reading to 500° is inserted in the brass block (B), so that the bulb is near the center. The top of the brass block is polished with sandpaper. The flames beneath

the block are adjusted by means of the air and gas attachments so that a nearly colorless flame is produced. The compound is finely powdered, and a very small amount is sprinkled on the center of the Maquenne block as the temperature is raised. If the compound does not melt immediately when it is dropped on the block it is removed with a piece of filter paper. A fresh sample is added after the temperature has risen, and this procedure of adding the powdered compound and wiping it off is repeated until a temperature is reached at which the powder melts instantaneously.

Special thermometers reading to 500° are available for use with the Maquenne block. This method, therefore, is the best for all high-melting compounds. It is also very valuable for compounds that gradually decompose as they are heated. The Maquenne block gives an instantaneous decomposition temperature whereas the capillary-tube method yields a value representing the melting point of a mixture of the original plus any decomposition

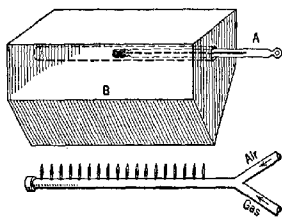


Fig. 3. Maquenne block.

products. It is for this reason that melting points determined by the capillary-tube method frequently differ from those determined by the Maquenne block method.

A more refined and very convenient form of the Maquenne block has been designed by Dennis and Shelton.¹ It is shown in Fig. 4.

The apparatus is set up so that the copper lead from the bar and the Constantan lead from the needle are attached to the potentiometer. The current through the resistance coil is adjusted by a rheostat so that the melting temperature of the material to be tested will occur at some point along the bar. The material, in powdered form, is then sprinkled lightly on the top of the bar, and it will be seen that there is a distinct line above which the material is molten and below which it is still solid. The needle is then pressed firmly onto the bar at this point, by the proper setting of the movable arm, and the temperature of this point may be read

¹ See Dennis and Shelton, *J. Am. Chem. Soc.*, **52**, 3128 (1930).

directly from the potentiometer. Only a small amount of the material is required, and, if desirable, it can be recovered upon completion of the test. The bar can easily be kept clean by

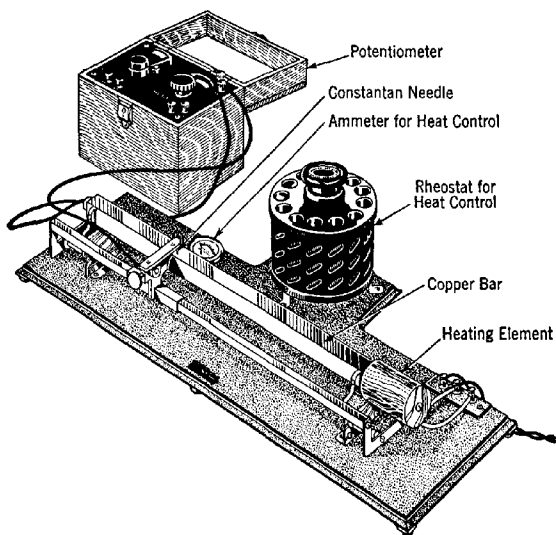


FIG. 4. Dennis melting-point apparatus. Reproduced by courtesy of the Burgess Parr Co., Moline, Illinois.

means of a small amount of metal polish. This apparatus is useful for determining melting points with an accuracy of 0.25° for compounds melting up to 300° .

Freezing Points

Procedure. A few milliliters of the liquid are placed in an ordinary test tube fitted with a thermometer and a wire stirrer (made of copper, nickel, or platinum). The tube is fastened in a slightly larger test tube by means of a cork and cooled in an ice or ice-salt bath or an acetone-Dry Ice mixture, and the liquid is stirred

vigorously (Fig. 5). As soon as crystals start to form the tube is removed from the bath, and vigorous stirring is continued while the temperature on the thermometer is being read. The freezing point is the temperature reached after the initial supercooling effect has disappeared.

Discussion. The temperature of the cooling bath should not be too far below the freezing point of the compound.

Question

Freezing points of most organic liquids as ordinarily determined are not very reliable. Why?

Boiling Points

Procedure A. A small-scale distillation apparatus similar to that shown in Fig. 6 is set up. It consists of a 25-ml. distilling flask placed on an asbestos board with a 2-cm. hole in the center. Test tubes immersed in a beaker of ice are used to condense the

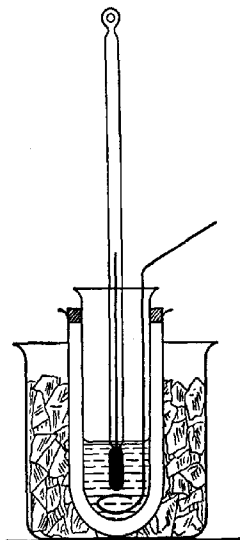


FIG. 5. Simple freezing-point apparatus.

vapors and act as receivers. A piece of clay plate is placed in the flask, and 10 ml. of the liquid whose boiling point is to be determined is added. The thermometer is inserted so that the top of the mercury bulb is just below the side arm. The liquid is heated to boiling by means of a low flame which should be protected from drafts by means of a properly placed shield. The liquid is distilled at as uniform a rate as possible. After the first 2 to 3 ml. of distillate has collected, the receiver is changed without interruption of the distillation, and the next 5 to 6 ml. is collected in a clean dry test tube. There will be a considerable lag of the thermometer reading, but usually the boiling-point range can be determined during the collection of the second portion of distillate. This boiling-point range should be recorded.

The boiling-point range is a useful index of purity of the sample. Many organic liquids are hygroscopic, and some decompose on standing. Generally the first few milliliters of distillate will contain any water or more volatile impurities, and the second fraction will consist of the pure substance. If the boiling-point range

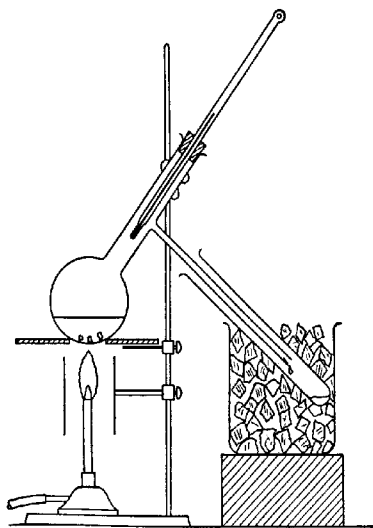


FIG. 6. Simple distillation apparatus.

is large, the liquid should be refractionated through a suitable column.

The boiling point determined by the distillation of a small amount of liquid as described above is frequently in error. Unless especial care is taken the vapor may be superheated; also the boiling points observed for high-boiling liquids may be too low because of the time required for the mercury in the thermometer bulb to reach the temperature of the vapor. The second fraction collected above should be used for a more accurate boiling-point determination by Procedure B or C. Portions of this same fraction should also be used for the determination of specific gravity, refractive index, or optical rotation.

Procedure B. When as much as 1 ml. of the pure anhydrous liquid is available its boiling point should be determined by means of the apparatus shown in Fig. 7. It consists of an ordinary Pyrex test tube, 16 by 150 mm. (A), fitted with a thermometer (T_1) by

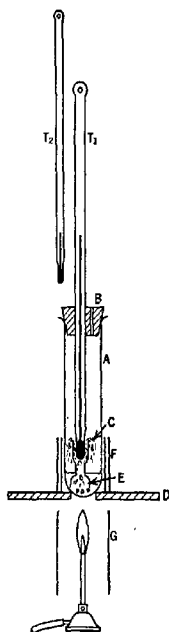


FIG. 7. Percolator boiling-point apparatus.

means of a cork (B) which has a slot to provide access to the air. The percolator cup (C) is made of glass tubing of such diameter that there will be about 1-mm. clearance between the bulb of the thermometer and the walls of the cup. Usually 8-mm. tubing will be suitable. The bottom of the cup flares outward so that it covers most of the bottom of the test tube, in which a few boiling stones (E) are placed. The test tube is insulated by two layers of asbestos paper (F) which extend 5 mm. above the height of the cup. The apparatus is mounted in a vertical position, the test tube being placed on an asbestos board (D) over a hole about 8 mm. in diameter. A second thermometer (T_2) is placed beside the first in order to get the temperature of the exposed mercury thread so that the stem correction may be calculated.

One milliliter of liquid is placed in the test tube, and the flame is adjusted so as to produce gentle boiling. The shield (G) protects the flame from drafts. The vapor should rise through the percolator cup carrying some liquid with it so that the mercury bulb is in contact with both liquid and vapor.

The liquid should boil vigorously enough so that the vapors rise about 1.0 cm. above the asbestos wrapping (F); the upper part of the test tube acts as a reflux condenser. The temperature (T_1) is read after equilibrium is reached (3-5 minutes). The auxiliary thermometer (T_2) is also read, and the stem correction is calculated and added to the reading on T_1 . The corrected boiling point is given by the following equation.

$$\text{B.P.} = T_1 + N(T_1 - T_2)0.000154$$

Procedure C. A micro boiling-point tube is made as shown in Fig. 8. The outer tube is made by sealing one end of a 5-mm. glass tube and cutting off a piece 5 cm. long. A capillary tube is sealed about 3 to 4 mm. from one end and placed in the larger tube (Fig. 8). Two drops of the liquid whose boiling point is to be determined are added, and the tube is fastened to the thermometer in the apparatus used for the determination of melting points (see Fig. 1). The temperature is raised until a rapid and continuous stream of bubbles comes out of the small capillary and passes through the liquid. The flame is then removed and the bath allowed to cool, while being stirred continuously. The temperature is noted at the instant bubbles cease to come out of the capillary and just before the liquid enters it. This temperature is the boiling point.

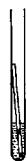


FIG. 8. Micro boiling-point tube.

At the time the boiling point is being determined the atmospheric pressure should be recorded. When the pressure is near 760 mm., the correction caused by a 10-mm. difference in pressure may be found by dividing the absolute boiling point by 850 for non-associated liquids (hydrocarbons, alkyl halides, ethers, esters) and by 1020 for associated liquids¹ (alcohols, acids). Table I illustrates the magnitude of such barometric corrections for pressures that do not differ from 760 mm. by more than about 30 mm.

TABLE I

B. P. °C.	B. P. Absolute	Correction in °C. for 10-mm. Difference in Pressure	
		Non-associated Liquids	Associated Liquids
50	323°	0.38	0.32
100	373	.44	.37
150	423	.50	.42
200	473	.56	.46
300	573	.68	.56
400	673	.79	.66
500	773	.91	.76

It is evident that small deviations in pressure from 760 mm., such as 5 mm., may be neglected in ordinary work.

¹ Smith and Menzies, *J. Am. Chem. Soc.*, **32**, 907 (1910).

Many different equations have been proposed for calculating the boiling points of organic liquids at reduced pressures. The integrated form of the Clausius-Clapeyron equation has been used along with Trouton's rule. This method has not proved to be generally satisfactory because Trouton's constant is not the same for associated and non-associated liquids; moreover, the degree of association varies with the temperature. This fact has led to the use of empirical equations in which different constants are

TABLE II
BOILING POINTS AT REDUCED PRESSURES

Compounds	Pressures in Millimeters of Mercury					T_{760} - T_{550}
	760	700	650	600	550	
<i>n</i> -Heptane	98° C.	96° C.	94° C.	91° C.	88° C.	10°
<i>n</i> -Propyl alcohol	97	95	93	91	89	8
Iodobenzene	188	185	182	179	175	13
<i>n</i> -Valeric acid	186	183	180	178	175	11
Fluorene	298	294	290	286	282	16
β -Naphthol	295	292	288	284	280	15

employed, depending on the class of compounds. One of the most useful is the equation developed by Hass and Newton¹ and converted by Bordenca² to a simple series of eight graphs corresponding to eight types of compounds.

Investigators working in laboratories at high altitudes and low barometric pressures have found it convenient to determine a set of empirical corrections to be added to observed boiling points in order to get boiling points at 760 mm. The corrections are obtained by distilling a number of different types of compounds with different boiling points. The difference between the boiling point recorded in the literature and the observed boiling point gives the correction.

A set of line-coordinate charts for the vapor pressure-temperature data of 183 organic compounds has been worked out,³ and these charts have been found to be very useful.

¹ Hass and Newton, *Handbook of Chemistry and Physics*, p. 1757, Chemical Rubber Company, Cleveland, Ohio (1945).

² Bordenca, *Ind. Eng. Chem., Anal. Ed.*, **18**, 99 (1946).

³ Germann and Knight, *Ind. Eng. Chem.*, **26**, 467 (1934).

In order to give an idea of the change in boiling point with pressure the data on three pairs of non-associated and associated compounds are given in Table II. The temperatures are given to the nearest whole degree.

The data indicate that, as the pressure is reduced, the boiling point of an associated compound does not fall off as much as the boiling point of a non-associated liquid.

Discussion. The boiling points of the members of a given homologous series increase as the series is ascended. The boiling points

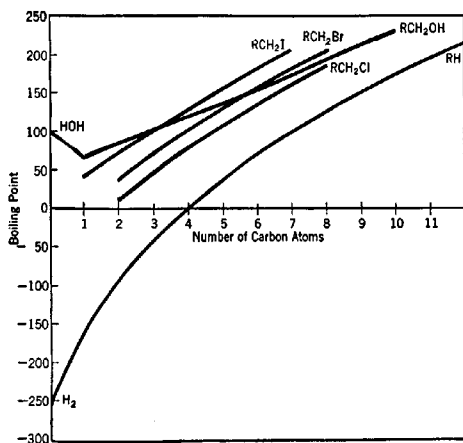


Fig. 9. Relationship of boiling points and molecular weight.

rise in a uniform manner as shown in Fig. 9, but the increment per $-\text{CH}_2$ group is not constant, being greater at the beginning of the series than for the higher members (Table III).

If a hydrogen atom of one of the paraffin hydrocarbons is replaced by another atom or group, an elevation of the boiling point results. Thus alkyl halides, alcohols, aldehydes, ketones, acids, etc., boil higher than the hydrocarbons with the same carbon skeleton.

If the group introduced is of such a nature that it promotes association, a very marked rise in boiling point occurs. This effect is especially pronounced in the alcohols (Fig. 9) and acids

since hydrogen bonding can occur. For example, the difference in boiling point between propane (non-associated) and *n*-propyl alcohol (associated) is 142°—a difference far greater than the

TABLE III

	B. P.	Δ
<i>n</i> -Pentane	36°	> 32
<i>n</i> -Hexane	68	> 30
<i>n</i> -Heptane	98	> 27
<i>n</i> -Octane	125	> 24
<i>n</i> -Nonane	149	> 24
<i>n</i> -Decane	173	> 21
<i>n</i> -Undecane	194	> 21
<i>n</i> -Dodecane	215	

change in molecular weight would indicate. As more hydroxyl groups are introduced the boiling point rises, but the change is not so great as that caused by the first hydroxyl group. The increment per hydroxyl group is much greater than the increment per methylene group (Table IV).

TABLE IV

CH ₃	CH ₃	CH ₂ OH	CH ₂ OH
CH ₂	CH ₂	CH ₂	CHOH
CH ₃	CH ₂ OH	CH ₂ OH	CH ₂ OH
-45°	+97°	+216°	+290°
$\Delta_{OH} = 142^\circ$		119°	74°

If the hydroxyl groups are converted to ether linkages, the association due to hydrogen bonds is prevented and the boiling point drops. The following series illustrates this effect.

CH ₂ OH	CH ₂ OC ₂ H ₅	CH ₂ OC ₂ H ₅	CH ₂ OC ₂ H ₅
CHOH	CHOH	CHOH	CHOC ₂ H ₅
CH ₂ OH	CH ₂ OH	CH ₂ OC ₂ H ₅	CH ₂ OC ₂ H ₅
+290°	+230°	+191°	+185°

A comparison of oxygen derivatives with their sulfur analogs also shows that association is a more potent factor than molecular

weight. The thiol compounds are associated only slightly and hence boil lower than their oxygen analogs even though the former have higher molecular weights than the latter.

	B. P.		B. P.
HOH.....	100°	HSH.....	-62°
CH ₃ OH.....	66	CH ₃ SH.....	+6
CH ₃ COOH.....	119	CH ₃ COSH.....	93

Ethers and thio ethers are not associated, and hence the alkyl sulfides boil higher than the ethers since they have a higher molecular weight.

	B. P.		B. P.
(CH ₃) ₂ O.....	-24°	(CH ₃) ₂ S.....	+38°
(C ₂ H ₅) ₂ O.....	+35	(C ₂ H ₅) ₂ S.....	92

These data on the sulfur and oxygen compounds, and on the hydrocarbons, alkyl chlorides, bromides, and iodides, illustrate the general rule that replacement of an atom by an atom of higher atomic weight causes a rise in the boiling point provided that no increase or decrease in the extent of association takes place as the result of this substitution.

Just as with solubility relationships (see p. 67), branching of the chain and position of the functional group influence the boiling point. The saturated aliphatic alcohols (Table V) serve to illustrate the following generalizations:

1. Among isomeric alcohols the straight-chain isomer has the highest boiling point.
2. If comparisons are made of alcohols of the same type, the greater the branching of the chain the lower the boiling point.
3. A comparison of the boiling points of isomeric primary, secondary, and tertiary alcohols shows that primary alcohols boil higher than secondary alcohols, which, in turn, boil higher than tertiary alcohols provided comparisons are made of isomeric alcohols with the same maximum chain length.

A knowledge of the boiling points of some simple compounds is frequently of value in excluding certain types of compounds. The following simple generalizations are helpful.

1. An organic chloro compound which boils below 132° must be aliphatic. If it boils above 132° it may be either aliphatic or

TABLE V

Primary Alcohols		Secondary Alcohols		Tertiary Alcohols	
Formulas	B. P.	Formulas	B. P.	Formulas	B. P.
CH_3OH	66°				
$\text{CH}_3\text{CH}_2\text{OH}$	78				
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	97	$\text{CH}_3\text{CH}(\text{CH}_3)\text{OH}$	82°		
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	116	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$	99	CH_3 $ \text{CH}_2-\text{C}-\text{CH}_3$ $ \text{OH}$	83°
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$	108				
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	138	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$	119		
$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$	131	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$	115		
$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$	129				
CH_3 $ \text{CH}_2-\text{C}-\text{CH}_2\text{OH}$ $ \text{CH}_3$	114	$\text{CH}_3\text{CH}-\text{CH}(\text{CH}_3)\text{OH}$	111	CH_3 $ \text{CH}_2\text{CH}_2-\text{C}-\text{CH}_3$ $ \text{OH}$	102

aromatic. This follows from the fact that the simplest aryl halide, chlorobenzene, boils at 132°.

2. Similarly, an organic bromo compound which boils below 157° or an iodo compound which boils below 188° must be aliphatic. Other bromo and iodo compounds may be either aliphatic or aromatic.

Questions

1. What corrections must be made for a boiling point determined by Procedure A? by Procedure B?
2. A narrow boiling-point range is not a reliable index of purity. Why?

Specific Gravity

Specific gravity may be determined by means of a small pycnometer or more conveniently by means of the Fisher-Davidson gravitometer.

Procedure for the Use of the Gravitometer. The principle of this instrument depends on the fact that, if two manometers contain-

ing liquids of different densities are connected to a common source of suction, the heights of the liquids are inversely proportional to their densities; see Fig. 10. Hence, if a liquid of known density is placed in one tube, the specific gravity of the liquid in the other tube may be calculated by measuring the heights of the two liquids.

The Fisher-Davidson gravimeter shown in Fig. 11 has been designed so that the height of one liquid varies in one tube only so that a single direct reading may be made. The instrument consists of two glass capillary tubes; one is L-shaped, and the other Z-shaped. They are connected at the top to a suction device which operates by varying the length of a rubber tube squeezed between rollers (shown by r, r in Fig. 10). If two liquids

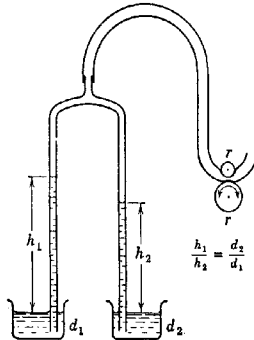


FIG. 10.

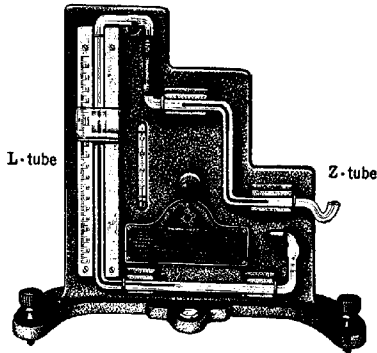


FIG. 11. Reproduced by courtesy of the Fisher Scientific Co., Pittsburgh, Pa.

are placed in the tubes and are drawn up by suction until the menisci in the Z-tube rest in the upper and lower horizontal parts, only one variable level will be observed, i.e., that in the L-tube

The instrument is made with a fixed height of the Z-tube so that, using ethylbenzene (sp. gr.²⁰/₄ = 0.867) as the reference liquid, the scale can be calibrated to read specific gravity directly.

In actual use, the ethylbenzene is introduced into the L-tube by means of a medicine dropper so that the liquid level stands between the two marks on the upturned end of the horizontal arm. No air bubbles should be in the column of liquid; if any appear they may be removed by driving the ethylbenzene back into the bulb. This is done by turning the milled knob controlling the suction counterclockwise as far as it will go, pinching the rubber connector between the L- and Z-tubes, and then rotating the knob in a clockwise direction. After the air bubbles are expelled, the tube is released and the knob turned clockwise as far as it will go. The Z-tube, which must be well cleaned and dry, is attached and clamped in the V-slots. The instrument is leveled by means of the adjusting screws in the legs, and the liquid whose specific gravity is to be determined is introduced into the cup at the end of the Z-tube. About 0.3 ml. is required to just fill the cup.

The milled knob is turned counterclockwise to suck the liquid into the Z-tube so that the menisci stand approximately in the middle of the upper and lower horizontal arms. The cursor with magnifier and vernier is moved up or down the scale opposite the L-tube until the index line is level with the meniscus of the ethylbenzene. The specific gravity is read to the third decimal place by means of the vernier; it represents the specific gravity at 20° compared to water at 4°. To ensure equilibrium, the liquid in the Z-tube should be moved slightly forward or backward by rotating the knob, and the reading of the ethylbenzene meniscus should be checked.

The sample is then returned to the cup by rotating the knob and removed by means of a medicine dropper. The Z-tube is disconnected, then washed with ethanol or acetone and ether. It is dried by drawing a slow stream of dry air through it. As long as the room temperature and that of the liquids are $20 \pm 5^\circ$, no temperature correction is necessary since most organic liquids have temperature coefficients which lie within a narrow range. The results are accurate to about 0.1%.

The standard Z-tube of 1.9-mm. bore is suitable for most liquids. For viscous liquids or aqueous solutions the 4-mm., and for liquids of very low viscosity the 0.8-mm. Z-tube should be used.

With ethylbenzene as the reference liquid the range of specific gravities which may be measured is 0.600 to 2.000. For liquids of higher specific gravity, carbon tetrachloride (sp. gr. $^{20}_4 = 1.595$) is used as the reference liquid, and the scale of readings is multiplied by 1.84.

Procedure for Pycnometer. If a small pycnometer with a capacity of 1 to 2 ml. is not available, either of the two forms shown in Fig. 12 or 13 may be made.

The pycnometer in Fig. 12 is made from a piece of glass tubing with a bore of 1 to 2 mm. It is bent into the shape shown, a small

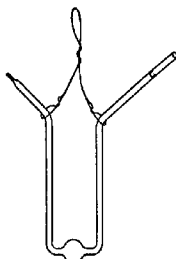


FIG. 12. Pycnometer.

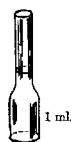


FIG. 13. Specific-gravity bulb.

bulb blown in the middle, and one end drawn out to a fine capillary. A scratch is made on the other arm at the same height as the tip of the capillary. The pycnometer is suspended by means of a fine Nichrome, aluminum, or platinum wire, and its weight is determined. The pycnometer is then filled with distilled water to a point beyond the mark and suspended in a beaker of water at 20° . After about 10 minutes, the amount of liquid in the tube is adjusted by holding a piece of filter paper to the capillary tip until the meniscus in the open arm coincides with the mark. The pycnometer is then removed from the beaker, dried, and weighed.

Figure 13 shows a small specific-gravity bulb. It is made by sealing a 5-mm. glass tube and blowing out the end into a small bulb. The bulb may be flattened by warming the bottom in a small blast flame and touching it with a spatula. A mark is made on the tube by means of a file or by etching. The weight of the empty bulb is determined. The tube is then filled with distilled water and suspended by a wire in a beaker of water at 20° . The

level of the water in the bulb is adjusted to the mark by means of a capillary pipet. The bulb is then removed from the beaker, dried, and weighed.

The weight of the empty pycnometer and its weight when filled with distilled water are recorded and kept permanently. To determine the specific gravity of a liquid the bulb or pycnometer is filled with the liquid at 20° and its weight determined.

$$\text{Sp. gr. } ^{20}/_{20} = \frac{\text{Weight of sample}}{\text{Weight of water}}$$

The apparatus must be carefully cleaned and dried immediately after use.

It is important that the sample used for this determination be pure. It is best to use a portion of the second fraction collected in the distillation experiment (p. 25). Sometimes it is necessary to determine the density with reference to that of water at 4°. This may be done by means of the factor 0.99823.

$$\text{Sp. gr. } ^{20}/_4 = \frac{\text{Weight of sample}}{\text{Weight of water}} \times 0.99823$$

Discussion. The specific gravity of a liquid may often be used to exclude certain compounds from the list of possibilities. It varies with the composition as well as the structure of the compound.

Hydrocarbons are usually lighter than water. As a given homologous series of hydrocarbons is ascended the specific gravity of the members increases, but the increment per methylene radical gradually diminishes. Curves I, II, and III in Fig. 14 show the change in density for the alkanes, 1-alkenes, and 1-alkynes. It will be noted that the specific gravity of the acetylenic hydrocarbon is greater than that of the corresponding olefin, which in turn is more dense than the paraffin hydrocarbon with the same number of carbon atoms. The position which the unsaturated linkage occupies also influences the density. Moving the double bond nearer the middle of the molecule causes an increase in the specific gravity. The data in Table VI illustrate this change.

Examination of Tables XXXIV, XXXV, and XXXVI in Chapter IX shows that most of the liquid hydrocarbons are lighter than water.

The replacement of one atom by another of higher atomic weight usually increases the density. Thus Curve IV, Fig. 14,

TABLE VI

Name	Compound	Sp. Gr.
1-Pentene	$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3$	0.645 ²⁵ / ₄
2-Pentene	$\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$	0.651 ²⁵ / ₄
1,4-Pentadiene	$\text{CH}_2=\text{CHCH}_2\text{CH}=\text{CH}_2$	0.659 ²⁰ / ₄
1,3-Pentadiene	$\text{CH}_2=\text{CHCH}=\text{CHCH}_3$	0.696 ²⁰ / ₄
2,3-Pentadiene	$\text{CH}_3\text{CH}=\text{C}=\text{CHCH}_3$	0.702 ²⁰ / ₄
1-Hexene	$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	0.673 ²⁰ / ₄
2-Hexene	$\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}_3$	0.681 ²⁰ / ₄
3-Hexene	$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_3$	0.722 ²⁰ / ₄

which represents the specific gravities of the normal alkyl chlorides, lies above that of the hydrocarbons. It will be noted that the

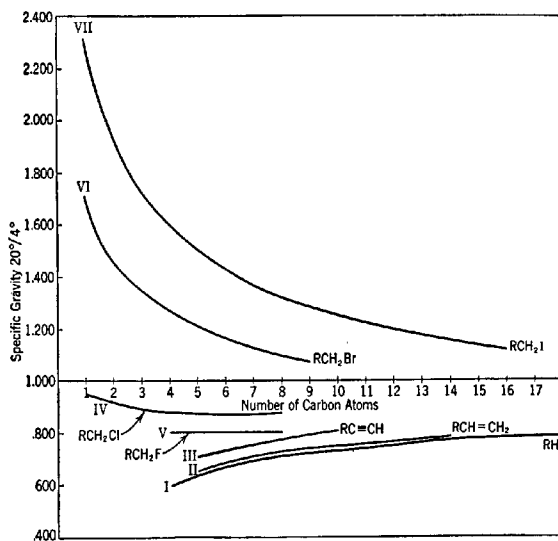


FIG. 14. Relationship of specific gravity and molecular weight.

alkyl chlorides are lighter than water and that the specific gravities decrease as the number of carbon atoms is increased.

The rather limited data on the alkyl fluorides are shown by Curve V, Fig. 14. This graph is interesting because it reveals only a very slight change in density as the number of carbon atoms is increased. Curve V represents the intermediate stage between Curves I and IV.

Curves VI and VII in Fig. 14 show that the specific gravity of the primary alkyl bromides and iodides is greater than 1.0 and that in these homologous series the specific gravity decreases as the number of carbon atoms is increased. The downward slope of Curves IV, VI, and VII is due to the fact that the halogen atom constitutes a smaller and smaller percentage of the molecule as the molecular weight is increased by increments of methylene radicals. The relative position of the curves in Fig. 14 shows that the specific gravity increases in the order



provided that comparisons are made on alkyl halides with the same carbon skeleton and of the same class. Similar relationships are exhibited by secondary and tertiary chlorides, bromides, and iodides.

The specific gravities of aryl halides also arrange themselves in the order of increasing weight of the substituent (Table VII).

TABLE VII

Compound	B. P.	Sp. Gr. ²⁰ / ₄
Benzene	79.6°	0.878
Fluorobenzene	86	1.024
Chlorobenzene	132	1.107
Bromobenzene	156	1.497
Iodobenzene	188	1.832

An increase in the number of halogen atoms present in the molecule increases the specific gravity. Compounds containing two or more chlorine atoms or one chlorine atom together with an oxygen atom or an aryl group will generally have a specific gravity greater than unity (Table VIII).

TABLE VIII

Benzyl chloride	1.1026 ¹⁸ / ₄	Carbon tetrachloride	1.595 ²⁰ / ₄
Benzal chloride	1.2557 ¹⁴ / ₄	Ethylene chlorohydrin	1.213 ²⁰ / ₄
Benzotrichloride	1.3800 ²⁰ / ₂₀	Chloroacetone	1.162 ¹⁶ / ₄
Methylene chloride	1.336 ²⁰ / ₄	Methyl chloroacetate	1.235 ²⁰ / ₂₀
Chloroform	1.4984 ¹⁵ / ₄		

The introduction of functional groups containing oxygen causes an increase in the specific gravity. The curves in Fig. 15 represent

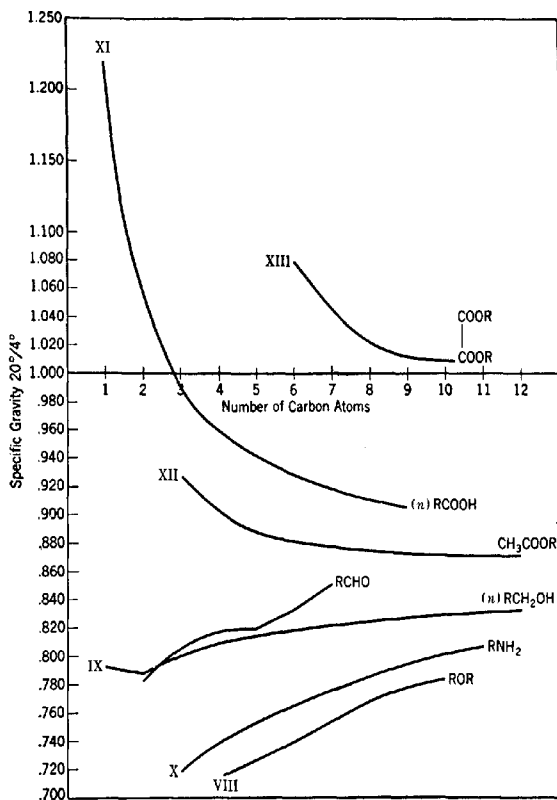


FIG. 15. Relationship of specific gravity and molecular weight.

the change in specific gravity of some of the common types of compounds.

The ethers (Curve VIII) are the lightest of all the organic oxygen compounds. The aliphatic alcohols (Curve IX) are heavier

than the ethers but lighter than water. The specific gravity of the alcohols becomes greater than 1.0 if a chlorine atom (ethylene chlorohydrin), a second hydroxyl (ethylene glycol), or an aromatic nucleus (benzyl alcohol) is introduced. The dip in Curve IX is due to the fact that methanol is more highly associated than ethanol. The amines (Curve X) are not so dense as the alcohols and are less associated. Association also causes the specific gravity of formic acid and acetic acid to be greater than unity; the higher liquid fatty acids are lighter than water (Curve XI).

The simple esters (Curve XII) are lighter than water whereas esters of polybasic acids (Curve XIII), halogenated, keto, or hydroxy esters are heavier than water. Introduction of the aromatic ring also may cause esters to be heavier than water. Examples of esters of these types which are heavier than water are phenyl acetate, methyl benzoate, benzyl acetate, ethyl salicylate, *n*-butyl oxalate, triacetin, isopropyl tartrate, and ethyl citrate. Since the hydrocarbons are lighter than water, it is to be expected that esters containing long hydrocarbon chains will show a correspondingly diminished specific gravity.

In general, compounds containing several functional groups—especially those groups that promote association—will have a specific gravity greater than 1.0. Merely noting whether a compound is lighter or heavier than water gives some idea of its complexity. This is of considerable value in the case of Classes N₁ and N₂ liquids. If the compound contains no halogen and has a specific gravity less than 1.0 it probably does not contain more than a single functional group in addition to the hydrocarbon or ether portion. If the compound is heavier than water it is probably polyfunctional.

The Index of Refraction

The refractive index of an organic liquid may be determined by means of a number of instruments;¹ among these may be mentioned the Pulfrich, immersion, Abbe, and Nichols refractometers. The last two types are useful in identification work because they require only a few drops of the compound, are simple to operate, and yield sufficiently accurate results.

¹ Bauer and Fajans, *Refractometry*, Chapter XVI in Vol. I, *Physical Methods of Organic Chemistry*, Interscience Publishers, New York, 1945.

Figure 16 is a schematic drawing showing the essential parts of an Abbe refractometer. Water at 20° from a constant temperature control apparatus is allowed to flow through the jackets (J) surrounding the prisms (P_1 , P_2) until they reach a temperature of 20° . The prisms are separated by opening the clamp (C), and a few drops of the pure liquid are placed on the ground-glass surface

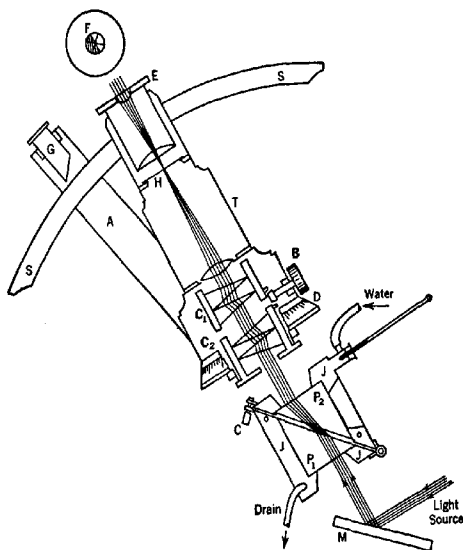


FIG. 16. Schematic diagram of an Abbe refractometer.

of the lower prism (P_1), which is then clamped to the upper polished prism (P_2). The instrument is set up so that light from a window or a frosted electric light bulb is reflected from M through the prisms (P_1 , P_2) up into the telescope (T). The reflector (M) may be a mirror or a sheet of plain white paper. The arm (A) is moved toward the lower end of the scale (S), and the angle of the telescope (T) and reflector (M) is adjusted so as to obtain a uniformly lighted field. The eyepiece (E) is focused on the cross hairs (H), and the arm (A) is moved so that the dividing line between the light and dark halves coincides with

the center of the cross hairs. Usually the borderline is colored and is achromatized by turning the milled screw (*B*) until a sharp black-to-white dividing line is obtained. This adjusting screw (*B*) rotates the two Amici prisms (*C*₁, *C*₂) which compensate for differences in the degree of refraction of light of different wave lengths present in white light. After the dividing line is made as sharp as possible, the arm (*A*) is moved by means of the micrometer screw attached to it so that the dividing line is exactly at the center of the cross hairs, as shown at *F*.

The index of refraction for the sodium D line is read directly from the scale (*S*, *S*) by means of the small magnifier (*G*). The result is recorded in the following form:

$$n_D^{20} = 1.4357$$

At the same time that the refractive index is read, the reading on the drum (*D*) should be noted. The prisms should then be cleaned with lens paper and acetone.

Procedure for the Use of the Nichols Refractometer.¹ The Nichols refractometer (Fig. 17) consists of a metal water jacket into which are inserted two cells (Fig. 18). Two models are available, which differ in the size of the cells.

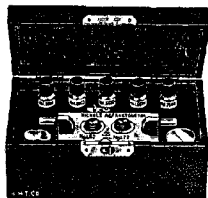


FIG. 17. Nichols refractometer, complete outfit consisting of macro model and accessories in case.

The macro size requires two to four drops of a liquid; the micro size, a droplet from a fine capillary micropipet. The construction and manipulation are the same. Each cell (Fig. 20) contains two matched prisms (*PP*) cemented to a glass disc (*D*) on which is engraved a fine line (*L*) protected by a glass cover (*G*). The sample (*S*) is placed in the cavity above the prisms and covered with the cover glass (*T*).

This instrument is placed on the stage of a microscope having a magnifying power of about 100 \times . Just above the diaphragm in the ocular is placed a ruled micrometer disc (Fig. 19). For ordinary use, white light from a frosted bulb is suitable for illumination. The light is reflected by the substage mirror

¹ Nichols, *Natl. Paint Bull.*, **1**, 12-14 (1937). Alder and Bryant, *Ind. Eng. Chem., Anal. Ed.*, **12**, 305 (1940).

up through the cell and the objective to the ocular. When the microscope is properly focused, two sharp lines (L_1 and L_2 in Fig. 19) are observed in the field, and the distance between these lines is measured by means of the lines ruled on the micrometer disc. The index of refraction is read from a calibration chart which must be prepared for each instrument and microscope.

The refractometer has two cells, one marked $n_D = 1.52$ and

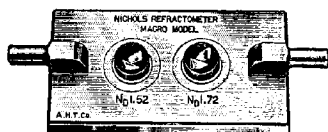


FIG. 18. Nichols refractometer, only, macro model.¹

the other $n_D = 1.72$. As a general guide the cell marked $n_D = 1.52$ should be used for liquids having refractive indices below 1.45 and above 1.60; the cell marked $n_D = 1.72$ should be used for values below 1.60 and above 1.80.

The calibration of each cell is carried out by filling the cell with a pure liquid of known refractive index. The cover glass is slid over the top, care being taken not to entrap air bubbles. Water

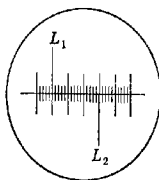


FIG. 19.

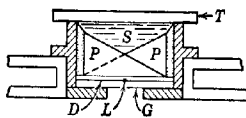


FIG. 20.

at 20° is circulated through the metal base. The microscope tube length is set at 160 mm., the light is adjusted, and the lines are brought into sharp definition by focusing the microscope in the usual way. The distance between the two lines is measured. The procedure is repeated for each of the five standard liquids supplied with the refractometer, and a graph is prepared by plotting the known refractive indices against the scale readings. The points

¹ Figures 17, 18, 19, and 20 are reproduced by courtesy of the Arthur H. Thomas Co.

will form a nearly straight line. From this graph the refractive indices of unknown liquids are read from the observed readings on the micrometer disc. In the same manner, a second calibration graph is prepared for the second cell. Care must be exercised to have the same light, ocular, objective, and tube length as for the calibration graphs.

The cell must be cleaned immediately after use. The liquid is removed by means of suction through a fine capillary pipet. Then the cell is washed twice with 95% ethanol (not with acetone) and finally with ether. The prisms are dried by a gentle stream of dry, filtered air from a capillary pipet. Since the evaporation of the ether cools the prisms, it is necessary to wait 3 to 5 minutes for temperature equilibrium to be established before a reading on a second liquid is taken. With ordinary white light the refractive index is determined with an accuracy of ± 0.001 . With monochromatic sodium light as the source of illumination and careful temperature control an accuracy of ± 0.0005 may be obtained.

Discussion. The values for density and refractive index are useful in excluding certain compounds from consideration in the identification of an unknown. Care must be taken, however, that the sample is pure. It is best to determine these physical constants on a portion of the distillate resulting from the determination of the boiling point.

These two constants can also serve as a final check on an unknown after its identity and structure have been established. They are of great value in research work for rapidly checking structures. This checking is accomplished by calculating the observed and theoretical molecular refractivities. The observed molecular refractivity is calculated by means of the Lorentz-Lorentz equation

$$M_D = \left(\frac{n^2 - 1}{n^2 + 2} \right) \left(\frac{m}{d} \right)$$

where n = refractive index, m = molecular weight, d = density. The theoretical molecular refractivity is the sum of the atomic refractivities plus exaltations due to unsaturation, ring forma-

tion, or special groups. The commonly used values are as follows.¹

ELEMENT	Na _D	NITROGEN IN	Na _D
C.....	2.42	Aromatic cyanides.....	3.79
H.....	1.10	Aliphatic oximes.....	3.93
O in OH.....	1.52	Amides.....	2.65
O in ester OR.....	1.64	Secondary amides.....	2.27
O=.....	2.21	Tertiary amides.....	2.71
Cl.....	5.96	NITRO GROUP IN	
Br.....	8.86	Alkyl nitrates.....	7.59
I.....	13.90	Alkyl nitrites.....	7.44
S in SH.....	7.69	Nitroparaffins.....	6.72
S in R ₂ S.....	7.97	Aromatic nitro compounds.....	7.30
S in RCNS.....	7.91	Nitramines.....	7.51
S in R ₂ S ₂	8.11	NITROSO GROUP IN	
NITROGEN IN		Nitrites.....	5.91
Hydroxylamines.....	2.48	Nitrosamines.....	5.37
Hydrazines.....	2.47	STRUCTURAL UNITS	
Primary aliphatic amines...	2.32	Double bond.....	1.73
Secondary aliphatic amines...	2.49	Triple bond.....	2.40
Tertiary aliphatic amines...	2.84	Three-membered ring.....	0.71
Primary aromatic amines...	3.21	Four-membered ring.....	0.48
Secondary aromatic amines...	3.59	Conjugation—Special values. Con-	
Tertiary aromatic amines...	4.36	sult literature.	
Aliphatic cyanides.....	3.05		

Dispersion. With the Abbe refractometer the reading of the drum (D) may be used in conjunction with the observed refractive index in obtaining the dispersion of the liquid. This value, v , is equal to $\frac{n_D - 1}{n_F - n_C}$ where n_D , n_F , and n_C are the refractive indices for the sodium D line, the blue hydrogen line, and the red hydrogen line, respectively. The dispersion values, v , are obtained by means of the dispersion chart supplied with each instrument and are characteristic for each compound. The partial dispersion, $n_F - n_C$, may also be calculated or obtained from tables, and from this the specific dispersion, δ , is obtained by dividing by the

¹ See Cohen, *Organic Chemistry*, Vol. II, pp. 17-40, 1921; Gilman, *Organic Chemistry*, Vol. II, p. 1751, 1943.

density taken at the same temperature. Usually the values are multiplied by 10,000 for convenience.

$$\delta^{20} = \frac{n_F - n_C}{d^{20}} \times 10^4$$

The specific dispersions have been found to be very useful since the values are characteristic for certain classes of compounds.¹ For example, all saturated hydrocarbons (paraffins, mono- or poly-cycloparaffins) have a value of about 99 ± 1 . The specific dispersions are not constant—for example, the alkylbenzenes range from 174 to 190; the alcohols from 68 to 90, etc.

The actual readings of the drum (frequently denoted as "Z" values) vary with instruments of different manufacture. However, for a given instrument these readings fall within certain ranges depending on the type of compound. On one of the Bausch and Lomb Abbe refractometers many colorless aliphatic compounds gave a reading approximating 17 whereas most colorless aromatic compounds gave a reading of about 24. Thus the magnitude of the Z value offers a possible means of distinguishing between aliphatic and aromatic compounds. It is necessary to determine the Z values for aliphatic and aromatic compounds for each instrument² since they vary considerably with the nature of the glass used in the prisms P_1 and P_2 and the compensating prisms C_1 and C_2 . Certain exceptions have been noted: carbon disulfide has a Z value of 40, and highly conjugated unsaturated compounds may also have Z values higher than would be expected. The rule cited above is to be interpreted, therefore, as holding for a considerable number of common organic compounds but not as an infallible generalization.

¹ Darmais, *Compt. rend.*, **171**, 952 (1920); **172**, 1102 (1921); Waterman and Perquin, *J. Inst. Petroleum Tech.*, **13**, 413 (1927); Vlugter, Waterman, and van Westen, *ibid.*, **21**, 661 (1935); Fuchs and Anderson, *Ind. Eng. Chem.*, **29**, 319 (1937); Ward and Kurtz, *Ind. Eng. Chem., Anal. Ed.*, **10**, 559 (1938); Wibaut, Hoog, Langedijk, Overhoff, and Smittenberg, *Rec. trav. chim.*, **58**, 329 (1939); Grosse and Wackher, *Ind. Eng. Chem., Anal. Ed.*, **11**, 614 (1939).

² On the Carl Zeiss Abbe type of refractometer aliphatic compounds give a drum reading of about 41 and aromatic compounds a value of about 35 (Jenkins, *Ind. Eng. Chem., Anal. Ed.*, **2**, 127 [1930]).

Optical Rotation

The optical rotation is determined only if the list of possible compounds contains optically active substances.

I. THE PREPARATION OF THE SOLUTION

Procedure. An accurately weighed sample (about 0.1 to 0.5 g.) of the compound is dissolved in 25 ml. of solvent in a volumetric flask. The solvents commonly used are water, ethanol, and chloroform. The solution should be clear; it must contain no suspended particles of dust or filter paper. It should also be colorless if possible. If the solution is not clear, either recrystallize the original compound or make up 50 ml. of the solution and filter through a small dry filter paper. The first 25 ml. of filtrate is discarded; the last 25 ml. is used for the determination.

II. FILLING THE POLARIMETER TUBE

Procedure. The cap is screwed on the small end of the tube, the tube held vertically, and the above solution poured in until the tube is full and the rounded meniscus extends above the top end of the tube. The glass plate is caused to slide over the end of the tube so that no air bubbles are imprisoned. The brass cap is then screwed on.

Precautions

1. A rubber washer should be placed between the glass plate and the brass cap. There is no washer between the glass end plate and the glass tube. This is a glass-to-glass contact.
2. The ends should not be screwed on too tightly. They should be turned up enough to make a firm, leak-proof joint. If the ends are screwed on too tightly the glass end plates are strained and a rotation will be observed with nothing in the tube at all. For substances with very low rotations it is advisable to loosen the caps and tighten them again between readings.
3. If the brass ends come off the glass tube they may be cemented in place again by means of litharge-glycerol cement. In putting an end back on be sure that the glass part extends 1 mm. beyond the brass end.

III. THE USE OF THE POLARIMETER

One form of the polarimeter is an instrument of the Lippich double-field type. A schematic diagram of the working parts is shown in Figs. 21 and 22.

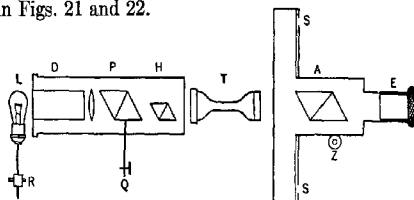


Fig. 21. Schematic diagram of Polarimeter (longitudinal section).

L = light } or replace with sodium flame
D = dichromate filter } or electric sodium lamp.
P = polarizing Nicol. *A* = analyzing Nicol.
Q = half-shadow adjustment. *E* = eyepiece.
H = half-shadow Nicol. *S* = scale.
T = tube containing solution. *R* = switch.

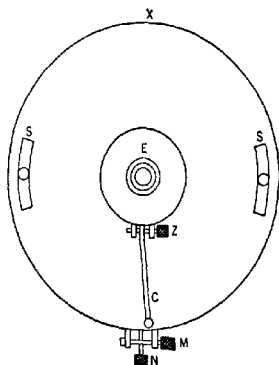


Fig. 22. Polarimeter (end view).

E = eyepiece.
Z = zero adjustment.
S = scale.
C = coarse adjustment.
N = locking nut.
M = micrometer adjustment.
X = lamp.

Procedure. The light (*L*) is turned on by means of snap switch *R*. The eyepiece (*E*) is focused by turning to right or left until the line dividing the two fields is sharp.

To determine the **zero reading** the locknut (*N*) is loosened and the two fields are matched approximately by means of the coarse adjustment lever (*C*). To use *C* it is necessary first to loosen *N* and then to tighten *C* by turning the white knob on the end of *C*. After approximate equality of the fields is obtained, *N* is tightened and the fields are matched exactly by turning the micrometer adjustment (*M*) to the right or to the left. The lamp (*X*) is turned on, and the scale (*S*) is read. The main circle is divided into degrees and 0.25 degree. The vernier or outside scale is divided into twenty-five divisions, enabling the reading to be made to 0.01 degree. At least five readings should be made and the values averaged. For very exact work both scales (*S*) should be read and the readings averaged in order to correct for any lack of centering of the scale with reference to the eyepiece and Nicols.

To get the **rotation** of the solution the polarimeter tube is placed in the trough. The cover is closed, and the procedure which was followed for the zero reading is repeated. The average of at least five readings should be taken. The observed rotation is the difference between this value and the zero reading.

Notes and Precautions

1. The instrument is usually set up for use with yellow light corresponding to the sodium D line. Light of this wave length is most readily obtained by means of electrically heated sodium lamps, which produce a brilliant yellow glow. A sodium flame may also be used, but it is not as brilliant. A white light using the following solution in a 3-cm. filter cell gives good results for compounds possessing low observed rotations. The filter solution is made of 8.9 g. of hydrated copper sulfate, 9.4 g. of potassium dichromate, and 300 g. of water. The solution is filtered and allowed to stand in order to permit dust particles to settle.

A mercury arc makes it possible for the green mercury line to be used. To use the green mercury line, the light (*L*) is removed and the dichromate filter (*D*) is unscrewed. The arc is substituted for *L*, and the above procedure is repeated.

2. The instrument is set up and adjusted for all ordinary work. The half-shadow lever (*Q*) or the zero screw (*Z*) should not be changed.

3. In making readings it is best to start with the scale (*S*) adjusted nearly to zero. If the arm (*C*) is moved very much, reversal of the fields will occur.

4. The lever (*C*) and locknut (*N*) should not be screwed up too tightly. It is only necessary to turn them up firmly.

IV. EXPRESSION OF RESULTS

The specific rotation of a substance is calculated by one of the following formulas:

For pure liquids:

$$[\alpha]_{\text{D}}^{25^{\circ}} = \frac{a}{ld}$$

For solutions:

$$[\alpha]_{\text{D}}^{25^{\circ}} = \frac{100a}{lc}$$

where $[\alpha]_{\text{D}}^{25^{\circ}}$ = specific rotation at 25°.

a = observed rotation.

l = length of tube (decimeters).

d = density.

c = grams in 100 ml. of solution.

Molecular Weight

The usual methods of determining molecular weights accurately are too cumbersome and time-consuming for rapid identification work. For compounds which have been described previously, molecular-weight determinations are unnecessary. In certain special cases where a derivative cannot be prepared or is unknown, the molecular weight may be determined conveniently by the Rast method.¹

Procedure. The weight of a small, clean, dry test tube (8 by 50 mm.) is determined. Approximately 50 mg. of the compound is placed in the tube and weighed accurately. Then about 0.5 g. of camphor is added and the tube again weighed. The contents of the tube are quickly melted by a very low flame to a clear liquid. (Caution: Do not heat too long.) After being cooled the contents of the tube are removed to a clean watch glass. The material is powdered and its melting point determined by the capillary-tube method. The capillary tube in which the melting point is determined should contain a column of the material only 1 mm. high, and the column must be tightly packed by means of a smaller capillary tube. That temperature is taken as the melting point at which the *solution* becomes entirely clear of solid. The melting point of the original camphor is determined. The difference in these melting points gives the depression in melting

¹ The original method was described by Rast, *Ber.*, **55**, 1051, 3727 (1922); subsequently, modifications have been suggested by Pirsch, *Ber.*, **65**, 862 (1932).

point of the camphor caused by the compound. The molecular weight is calculated by the formula

$$M = \frac{39.7 \times w \times 1000}{\Delta \times W}$$

where w = weight of compound.

W = weight of camphor.

Δ = the depression in the melting point.

Discussion. The above method depends on the fact that the molar lowering in the melting point of camphor is very large. A study¹ has shown that the value of 39.7 for the molar depression constant K for *d*-camphor holds for solute concentrations above 0.2 molar. More dilute solutions cause an increase in the constant to about 50. Consequently it is necessary to run a preliminary molecular-weight determination on an unknown compound and calculate an approximate molecular weight. Then a second determination is carried out, using an amount of the solute such that a 0.2 to 0.5 molar solution of the solute in camphor results.

Pirsch has suggested the use of the following compounds as solvents for molecular-weight determinations.

	Melting Point	Molecular Depression
Camphene	49°	31.08
Pinene hydrochloride	124	45.40
Pinene dibromide	170	80.9
Borneol	204	35.8

A technic for the determination of the molecular weights of volatile liquids has been described by Pirsch.²

Questions

1. What are the limitations of methods for determining molecular weights by the lowering of the freezing point?
2. If a compound decomposes at 100°, which of the above substances should be used as the solvent for determination of the molecular weight?
3. Which of the above solvents would yield the most accurate results?

¹ Meldrum, Saxer, and Jones, *J. Am. Chem. Soc.*, **65**, 2023 (1943); Ricci, *ibid.*, **66**, 658 (1944).

² For detailed directions see Pirsch, *Ber.*, **65**, 865 (1932).

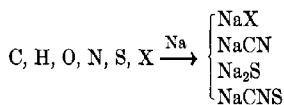
CHAPTER V

QUALITATIVE ANALYSIS FOR THE ELEMENTS

The elements commonly occurring along with carbon, hydrogen, and oxygen are nitrogen, sulfur, fluorine, chlorine, bromine, and iodine.

The detection of these elements depends on converting them to water-soluble ionic compounds and the application of specific tests.

Fusion of Organic Compounds with Metals



Caution. A few classes of organic compounds such as nitroalkanes, organic azides, diazo esters, diazonium salts, and some aliphatic polyhalides (chloroform, carbon tetrachloride) react explosively with hot sodium or magnesium. *Safety goggles always should be worn when these decompositions are being carried out.*

If a sharp report or explosion occurs when the first portion of the unknown is heated with the sodium, the procedure is interrupted and about 0.5 g. of the unknown is reduced by boiling gently with 5 ml. of glacial acetic acid and 0.5 g. of zinc dust. After most of the zinc has dissolved, the mixture is evaporated to dryness and the entire residue is then decomposed by Procedure A or B below.

Procedure A. Sodium.¹ A small test tube (50 by 8 mm.) is fastened in a vertical position in a Bunsen clamp from which the rubber has been removed. A piece of clean sodium metal about the size of a pea is placed in the test tube, and a little of the com-

¹ For a good discussion of the Lassaigne sodium decomposition test see Tucker, *J. Chem. Education*, **22**, 212 (1945).

pound is added. The lower part of the tube is heated until the sodium melts and the sodium vapors rise in the tube. Then more of the compound is added, and heat is again applied. The addition and heating are repeated a second time, and then the bottom of the tube is heated to a dull red heat. The tube is allowed to cool, and 1 ml. of ethanol is added to dissolve any unchanged sodium. The tube is heated again and while still hot is dropped into a small beaker containing 20 ml. of distilled water (caution). The tube is broken up with a stirring rod, and the solution is heated to boiling and filtered. The filtrate, which should be colorless, is used for the specific tests described below.

Procedure B. *Magnesium and Potassium Carbonate.*¹ Prepare the fusion mixture by grinding together 2 parts of anhydrous potassium carbonate and 1 part of magnesium powder. Place about 0.1 g. of the compound to be tested in the bottom of a small (8 by 50 mm.) dry test tube. If the substance is a liquid it is best added by means of a pipet, so as not to wet the walls of the test tube. Clamp the tube at an angle of about 30° from the horizontal, and allow 0.2 g. of the magnesium-potassium carbonate mixture to slide down the side of the test tube. This mixture should extend about 3 cm. up the tube and come within 1 cm. of the sample. Allow 2 drops of ether to run down on the mixture, and plug the mouth of the tube with glass wool.

Start heating the mixture with the Bunsen burner near the mouth of the tube. When the mass begins to glow, bring the lower end of the tube into the flame so as to distil the compound over the glowing mass.

The compound in the test tube must not be heated until the reaction between the carbonate and magnesium has started. The magnesium-potassium carbonate mixture must be a glowing red.

Continue heating, and finally bring the whole tube to a dull redness. Then drop the hot tube into 20 ml. of distilled water in a beaker. Break up the tube, stir the mixture thoroughly, and filter. The filtrate is used for the subsequent tests.

Sulfur. A few milliliters of the above solution is acidified with acetic acid, and a few drops of lead acetate solution are added. A black precipitate of lead sulfide indicates sulfur.

¹ Baker and Barkenbus, *Ind. Eng. Chem., Anal. Ed.*, **9**, 135 (1937).

To another milliliter of the solution 2 drops of a solution of sodium nitroprusside are added. A deep reddish-violet coloration indicates sulfur.

Nitrogen. (A) About 3 ml. of the stock solution is acidified with acetic acid; 2 drops of a 1% solution of benzidine in 50% acetic acid is added, and the mixture is stirred. The addition of 1 drop of a 1% copper sulfate solution produces a blue color or a blue precipitate if nitrogen is present. Chlorides and bromides do not yield colors, but iodides give a greenish precipitate. If both nitrogen (as cyanide) and iodides are present the precipitate is blue.

(B) About 2 drops of ammonium polysulfide solution is added to 2 ml. of the stock solution, and the mixture is evaporated to dryness on the steam bath. Dilute hydrochloric acid (5 ml.) is added, and the solution is warmed and filtered. A few drops of ferric chloride solution are added to the filtrate. A red coloration indicates nitrogen.

(C) A few crystals of sodium nitrite are dissolved in 3 ml. of the stock solution, 2 drops of ferric chloride solution are added, and the resulting solution is acidified with dilute sulfuric acid. The mixture is heated to boiling, made alkaline with ammonia, and filtered. The addition to the filtrate of 1 drop of hydrogen sulfide water or alkali sulfide produces a violet color in the presence of nitrogen.

(D) To 5 ml. of the filtrate add 5 drops each of 10 per cent sodium hydroxide solution, 4 per cent ferrous ammonium sulfate solution, and 20 per cent potassium fluoride solution.¹ Heat the mixture to boiling, and boil gently for about 30 seconds. If sulfur has been found to be present, the solution is filtered from the precipitate of iron sulfide. Then cool the tube containing the filtrate by holding it under a stream of running water. Add 1 drop of 5 per cent ferric chloride solution, and acidify the solution with dilute (6 N) sulfuric acid until the iron hydroxide just dissolves. The appearance of the characteristic precipitate of Prussian blue indicates the presence of nitrogen.

This precipitate may best be observed if it is collected and washed on white filter paper. If no precipitate is observed but a blue or greenish-blue solution is obtained, probably the original sodium decomposition was not complete. Another sodium decom-

¹ Viehoveer and Johns, *J. Am. Chem. Soc.*, **37**, 604 (1915).

position should be made using larger amounts of materials. Mixing the compound with an equal weight of powdered sucrose before the sodium decomposition and fusing this mixture with sodium will often assist in converting the nitrogen to sodium cyanide.

The test for nitrogen is often unsatisfactory, but indications of its presence may frequently be obtained as a result of solubility determinations or classification reactions. It is especially difficult to obtain a test for nitrogen from a nitro compound. The nitro group may be detected by the fact that most nitro compounds give a deep red color with alkalis. Many organic compounds containing nitrogen liberate ammonia when heated in a small test tube with soda-lime. The ammonia may be detected by its odor or by means of a piece of moist red litmus paper held in the mouth of the tube.

The Halogens. (A) About 2 ml. of the solution is acidified with dilute nitric acid and boiled gently for a few minutes to expel any hydrogen cyanide or hydrogen sulfide that may be present. A few drops of silver nitrate solution are added. A heavy precipitate indicates the presence of chlorine, bromine, or iodine. If only a faint turbidity or opalescence is produced it is probably due to the presence of impurities in the reagents or in the glass of the test tube used in the original sodium decomposition.

(B) Beilstein's Test. A small loop is made in the end of a copper wire and is heated in the Bunsen flame until the flame is no longer colored. The wire is cooled; the loop is dipped in a little of the original compound and heated in the edge of the Bunsen flame. A green flame indicates halogen.

This test is extremely sensitive and should always be confirmed by the silver nitrate test since minute traces of impurities containing halogen suffice to produce a green flame. Very volatile liquids may evaporate completely before the wire can be heated sufficiently to cause decomposition, thus causing failure of the test.

It has been stated that certain compounds not containing halogen cause a green color to be imparted to the flame. Among the compounds listed are quinoline and pyridine derivatives, organic acids,¹ urea, and copper cyanide.²

(C) Bromine and Iodine. About 3 ml. of the solution from the sodium decomposition is acidified with dilute sulfuric acid and

¹ Gilman and Kirby, *J. Am. Chem. Soc.*, **51**, 1575 (1929).

² See van Alphen, *Rec. trav. chim.*, **52**, 567 (1933).

boiled for a few minutes. The solution is cooled, and 1 ml. of carbon tetrachloride is introduced; then a drop of freshly prepared chlorine water¹ is added. The production of a purple color in the carbon tetrachloride indicates iodine. The addition of chlorine water is continued drop by drop, the solution being shaken after each addition. The purple color will gradually disappear and will be replaced by a reddish-brown color if bromine is present.

(D) *Bromine.* To 3 ml. of the stock solution in a test tube are added 3 ml. of glacial acetic acid and 0.1 g. of lead peroxide. A piece of filter paper, moistened with the fuchsin-aldehyde reagent (p. 101), is placed over the mouth of the test tube, and the contents of the tube are heated to boiling. If bromide is present in the solution, the vapors of bromine turn the paper violet. Chlorides, cyanides, and iodides do not produce any color.

A piece of filter paper dipped in a 1% alcoholic solution of fluorescein may be used in place of the fuchsin-aldehyde reagent. The bromine vapors cause the yellow fluorescein to turn pink owing to the formation of eosin. Chlorides, iodides, and cyanides do not interfere with this test.

(E) *Chlorine.* If the above tests for bromine and iodine are negative and a good precipitate was produced by silver nitrate the presence of chlorine is indicated. If bromine and iodine have been found to be present, one of the following procedures should be used to detect the presence of chlorine.

(F) *Chlorine, Bromine, and Iodine.* About 10 ml. of the stock solution is acidified with dilute sulfuric acid and boiled for a few minutes. The solution is cooled and tested for iodine by adding 0.5 ml. of carbon tetrachloride to 1 ml. of the solution and adding a few drops of sodium nitrite solution. A purple color indicates iodine. If iodine is present the remainder of the solution is treated with sodium nitrite and the iodine is extracted with carbon tetrachloride. The solution is finally boiled for a minute and then cooled. To 1 ml. of this solution, 0.5 ml. of carbon tetrachloride and 2 drops of chlorine water¹ are added. A brown color indicates bromine. The remaining solution is diluted to 60 ml., 2 ml. of concentrated sulfuric acid and then 0.5 g. of potassium persulfate are added, and the solution is boiled for 5 minutes. After the mixture has been cooled, silver nitrate solution is added; a white precipitate indicates chlorine.

¹ Since chlorine water does not keep well, a stabilized sodium hypochlorite such as "Chlorox" may be used, but the test solution must be kept acid to litmus.

A similar procedure for the detection of chlorine, in which lead peroxide and acetic acid replace potassium persulfate and sulfuric acid as the oxidizing agent, may also be used.

(G) *Chlorine*¹ *in the Presence of Nitrogen, Sulfur, Bromine, and Iodine.* About 10 ml. of the original stock solution is acidified with dilute nitric acid and boiled to expel hydrogen cyanide and hydrogen sulfide. Sufficient silver nitrate is added to precipitate completely all the halogens as silver halides, and the precipitate is removed. If both nitrogen and sulfur are present, the precipitate is boiled for 10 minutes with 30 ml. of concentrated nitric acid to destroy any silver thiocyanate that may be present. The mixture is then diluted with 30 ml. of distilled water and filtered. The precipitate of silver halides is then boiled with 20 ml. of 0.1% sodium hydroxide for 2 minutes. The solution is filtered, the filtrate is acidified with nitric acid, and silver nitrate solution is added. A white precipitate indicates chlorine.

(H) *Fluorine.* (a) About 4 ml. of the stock solution is acidified with acetic acid. The solution is boiled and cooled, and 2 to 5 drops of saturated calcium chloride solution are added. If fluorine is present a gelatinous precipitate of calcium fluoride will form when the solution is allowed to stand for several hours.

(b) About 2 ml. of the stock solution is acidified with acetic acid, and the solution is boiled and cooled. One drop of the solution is placed on a piece of zirconium-alizarin test paper. A yellow color on the red paper indicates the presence of fluoride. The test paper is prepared by dipping a piece of filter paper into a solution composed of 3 ml. of 1% alcoholic alizarin solution and 2 ml. of a 0.4% solution of zirconium chloride (or nitrate). The red filter paper is dried and, just before use, is moistened with a drop of 50% acetic acid.

¹ Reedy, *Elementary Qualitative Analysis*, McGraw-Hill Book Co., New York, 1941.

CHAPTER VI

THE SOLUBILITY CLASSES

The number of organic compounds is so large that it is necessary for identification purposes to establish numerous subdivisions. In the scheme used in this text, such a subdivision is accomplished by reference to "solubility" in various liquids: namely, water, ether, 5% sodium hydroxide solution, 5% sodium bicarbonate solution, 5% hydrochloric acid, cold concentrated sulfuric acid, and 85% phosphoric acid. Water and ether will be spoken of as "inert solvents"; the others, as "reaction solvents."

The system of classification is shown in Fig. 23. Compounds are divided at the outset into two great groups according to their solubility in water. Each of these groups is then subdivided by the use of the other solvents. The water-soluble compounds are divided into two classes: those soluble in ether (Class S_1) and those insoluble in ether (Class S_2).

By use of 5% sodium hydroxide solution and 5% hydrochloric acid, the compounds of the water-insoluble group are subdivided into three categories: acidic, basic, and neutral compounds. The acidic compounds are separated into two classes by reference to their solubilities in sodium bicarbonate solution. Class A_1 includes those that are soluble and Class A_2 those that are insoluble in this reagent. The basic compounds are not divided further: they form Class B.

The problem of classifying neutral compounds is simplified greatly by making a separation on the basis of differences in elementary composition. Compounds containing elements other than carbon, hydrogen, oxygen, and the halogens are placed in Class M. This class comprises a miscellaneous collection of compounds containing nitrogen, sulfur, and other elements of less common occurrence.

The remainder of the neutral compounds are subdivided by use of sulfuric acid. Those that are insoluble—the inert compounds—form Class I. The soluble compounds are classified further by reference to their solubility in syrupy phosphoric acid and are

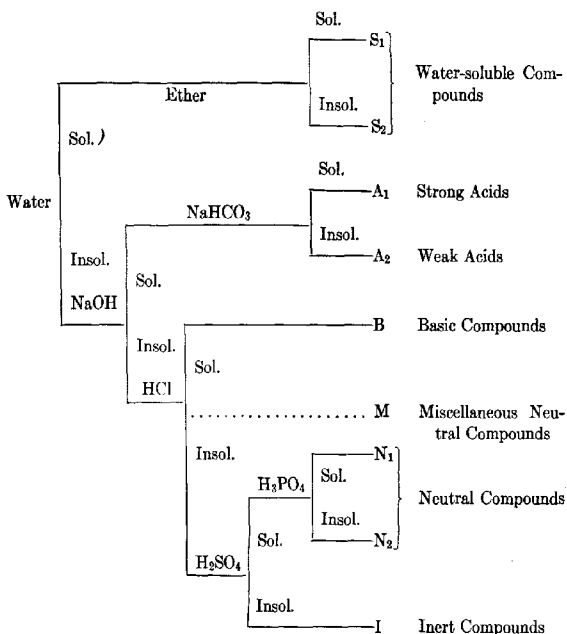


FIG. 23. Division of organic compounds into solubility classes.

put in Class N₁ or Class N₂, depending, respectively, on whether they are soluble or insoluble in this acid.

The solubility tests necessary for the classification of the various types of compounds are shown in Table IX.

From Table IX it is apparent that in identifying a compound an enormous advantage may be gained by first assigning it to one of the nine solubility classes. This will be made clearer if each class is considered separately.

TABLE IX

Class	Water	Ether	NaOH	NaHCO ₃	HCl	H ₂ SO ₄	H ₃ PO ₄
S ₁	+	+					
S ₂	+	-					
A ₁	-		+	+			
A ₂	-		+	-			
B	-				+		
M	-				-		
N ₁	-		-		-	+	+
N ₂	-		-		-	+	-
I	-		-		-	-	

* + denotes solubility; - denotes insolubility.

† If a compound contains nitrogen its solubility in hydrochloric acid should be tested also to see whether it is amphoteric. If it is soluble in hydrochloric acid much can be gained by placing it in Class A₁(B) or A₂(B).

Class S₁. Compounds soluble in water and ether. In this class are found almost all compounds of low molecular weight. Exceptions are low-molecular-weight hydrocarbons and their halogen derivatives, which fall in Class I. Low-molecular-weight compounds that have two or more functional groups usually belong in Class S₂.

Class S₂. Compounds soluble in water and insoluble in ether. Water-soluble salts of all kinds, most of the low-molecular-weight bifunctional compounds, and many polyfunctional compounds are in this class.

Class A₁. Compounds insoluble in water but soluble in sodium hydroxide solution and in sodium bicarbonate solution. Acids and a few negatively substituted phenols, such as picric acid and *s*-tribromophenol, make up this class.

Class A₂. Compounds insoluble in water and in sodium bicarbonate solution and soluble in sodium hydroxide solution. Weakly acidic compounds belong in this class. Weakly acidic properties usually are exhibited by oximes, imides, amino acids, sulfonamides of primary amines, primary and secondary nitro compounds, enols, and phenols. Certain mercaptans also are weak acids.

Class B. Compounds, insoluble in water and in alkali, which react with dilute hydrochloric acid to yield soluble products. Amines are in this class. Diaryl- and triarylamines are exceptions, being nearly neutral compounds. Amphoteric compounds are classed as A₁(B) or A₂(B). Water-insoluble salts of weak

acids such as calcium oxalate also are in Class B. Likewise certain acetals, which are readily hydrolyzed by dilute acids, may fall in this class.

Class M. Neutral compounds, insoluble in water, which contain elements other than carbon, hydrogen, oxygen, and the halogens. Nitro compounds, amides, negatively substituted amines, nitriles, azo compounds, hydrazo compounds, sulfones, sulfonamides derived from secondary amines, mercaptans, thio ethers, and many less common types of compounds are classified in the miscellaneous group.

Class N₁. Neutral compounds insoluble in water and soluble in sulfuric acid and in phosphoric acid. Low-molecular-weight alcohols, aldehydes, cyanones, methyl ketones, and esters make up this class. In most of these series the upper limit of solubility in phosphoric acid is in the neighborhood of the members containing nine carbon atoms.

Class N₂. Neutral compounds insoluble in water and in syrupy phosphoric acid and soluble in sulfuric acid. In addition to alcohols, aldehydes, cyanones, ketones, and esters which have more than nine carbon atoms this class contains many quinones, ethers, and unsaturated hydrocarbons. Anhydrides, lactones, and acetals may be found here as well as in Classes S₁ and N₁.

Class I. Compounds, insoluble in water, which dissolve in none of the reaction solvents. Saturated aliphatic hydrocarbons, aromatic hydrocarbons, and halogen derivatives of these hydrocarbons constitute the inert class.

DETERMINATION OF THE SOLUBILITY CLASS

A. Experiment on Known Compounds

Place 0.2 ml. (0.1 g. of a solid) of the compound in a test tube, and add in portions 3 ml. of water. Shake vigorously after the addition of each portion of solvent, being careful to keep the mixture at room temperature. If the compound dissolves completely, record it as soluble. In the same way test the solubility of the compound in other solvents, taken in the order shown in Table IX, until the solubility class is found.

By means of the foregoing procedure, determine the solubility class of each of the following compounds: (1) toluene, (2) benzyl

alcohol, (3) ethyl acetate, (4) acetanilide, (5) sucrose, (6) ethyl benzoate, (7) dimethylaniline, (8) phthalimide, (9) benzonitrile, (10) anthranilic acid. Tabulate the results as shown in Table X. In that table, + denotes solubility, - insolubility, and \pm a doubtful or borderline case. All results of the last type should be checked by a second determination.

DISCUSSION

Solids should be finely powdered to increase the rate of solution. If the solid appears to be insoluble in water or ether it is sometimes advisable to heat the mixture gently. If solution is effected in this way the liquid again is cooled to room temperature and is shaken to prevent supersaturation. It is always well in such cases to "seed" the cooled solution by adding a crystal of the solid. Especial care should be taken in weighing the sample; it should weigh 0.10 g. within 0.01 g.



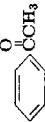

Liquids are handled most conveniently by means of a graduated pipet which permits accurate measurement of the amount added.

When the solubility in acid or alkali is being determined heat should not be applied since it might cause hydrolysis to occur. If the mixture is shaken thoroughly the time required for solution to take place should not be more than 1 or 2 minutes.

In the case of reaction solvents, it frequently is more expeditious and more economical to place the 3 ml. of solvent in the test tube and add the solute portionwise. Thus if a compound is very insoluble the fact may be established by use of only a very little of the substance, and the amount will not need to be weighed or measured. In general, where rough tests of solubility are adequate, the prescribed procedure may be simplified greatly, but whenever any doubt exists the solubility determinations should be made accurately.

Often it is possible to utilize a single portion of solute for tests with several different solvents. Thus if the compound is found to be insoluble in water one may get a fairly accurate measure of its solubility in dilute sodium hydroxide solution by adding about 1 ml. of a 20% solution of sodium hydroxide. The resulting 4 ml. of solvent will contain about 5% of sodium hydroxide. If the substance is very insoluble it often may be recovered and used subsequently for the hydrochloric acid test.

TABLE X

Name	Structural Formula	Solubility in							Class
		Water	Ether	NaOH	NaHCO ₃	HCl	H ₂ SO ₄	H ₃ PO ₄	
Catechol		+	+						S ₁
<i>o</i> -Cresol		-		+	-				A ₂
Carbon disulfide	CS ₂	-		-		-			M
<i>n</i> -Hexane	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	-		-		-	-		I
Acetophenone		-		-		-	+	+	N ₁
Allyl acetate		±	+	±		±	+	+	S _T -N ₁

When phosphoric and sulfuric acids are used it is more convenient to place the 3 ml. of solvent in the test tube and then add the solute. With these reagents significant reactions sometimes take place, and it is important to look for such manifestations as the production of heat, change of color, the formation of a precipitate, or the evolution of a gas. Careful notes should be made of all such observations since they may be very useful at a later stage of the identification.

B. Experiment on Unknown Compounds

For this experiment eight unknown compounds will be obtained from the instructor. The unknown compounds are to be classified in the same manner as the known compounds in Experiment 1, and the data are to be tabulated as in Table X. Since the elementary composition of the unknown compounds is not determined, Class M compounds are not included in this experiment. When the classification has been completed this table is to be transferred in ink to a report sheet and submitted to the instructor.

The names of the compounds will be supplied to the student after he has turned in his report. When he receives his report from the instructor the student will complete the table by placing the names and formulas in the spaces reserved for them.

DEFINITION OF SOLUBILITY

When a mixture of a specified amount of a given solvent and a specified amount of a given solute forms a homogeneous liquid the solute is said to be soluble in the solvent. This definition of solubility, adopted in this work for practical reasons, does not take into account the reason for the result or concern itself with the nature of the process; it makes no attempt to differentiate between solutions due to physical properties and those that depend on a chemical reaction. Undoubtedly both classes exist, and in a very large number of cases solution is due to a combination of physical and chemical forces.

Reactions with the solvent may result in complete solution or cause the formation of a product which is insoluble. Compounds of the latter type are best classified as soluble. For example, certain arylamines, such as α -naphthylamine, form hydrochlorides which are sparingly soluble in dilute hydrochloric acid. By

warming the mixture slightly and diluting it with water, solution sometimes may be effected. The appearance of the solid usually will show whether the amine has undergone a change. In order to decide doubtful cases, the solid should be separated and its melting point compared with that of the original compound. A halogen test with alcoholic silver nitrate would indicate formation of a hydrochloride. Compounds which form slightly soluble hydrochlorides are placed in Class B. Many secondary and tertiary alcohols are dehydrated readily by concentrated sulfuric acid to give olefins which then undergo polymerization. The resulting polymers are insoluble in cold concentrated sulfuric acid and hence form a distinct layer on top of the acid. Alcohols exhibiting this behavior are considered soluble and placed in Class N_1 or N_2 . Benzyl alcohol and its substitution products dissolve in concentrated sulfuric acid, which causes condensation to form orange-colored insoluble precipitates. Such compounds are classified as soluble and placed in Class N_1 or N_2 .

Low-molecular-weight esters of formic and pyruvic acids are hydrolyzed by water at room temperature as indicated by the fact that the aqueous solution becomes distinctly acid to litmus. They dissolve in ether without reaction and are placed in Class S_1 .

Esters containing five or six carbon atoms that are almost completely soluble in water may be hydrolyzed by continued shaking with dilute sodium hydroxide solution. The alkali should not be heated, and the solubility or insolubility should be recorded after 1 to 2 minutes.

Fatty acids containing twelve or more carbon atoms react with alkali slowly, forming sodium salts which are soaps. The mixture is not clear but consists of an opalescent colloidal dispersion that foams when shaken. Once this behavior has been observed it is easily recognized. Such acids are placed in Class A_1 .

GENERALIZATIONS

By the study of solubility data it has been found possible to lay down certain generalizations which often enable one to predict the solubility class of a compound merely by inspection of its structural formula. These generalizations have many exceptions, however, so that in this outline they have been supplemented by a table of solubilities in which are listed the more

common compounds whose solubility classes cannot be predicted with certainty.

Solubility in Water. Since water is a polar compound its solvent power is closely related to the polar character of the solute, which depends in turn on the number and nature of its functional groups. Olefinic and acetylenic linkages or benzenoid structures do not affect the polarity greatly. Hence, unsaturated or aromatic hydrocarbons are not very different from the paraffins in their water solubility. The introduction of halogen atoms does not alter the polarity appreciably. It does increase the molecular weight, and, for this reason, the water solubility always falls off. On the other hand salts are extremely polar, the ones encountered in this work generally being water soluble.

Other compounds lie between these two extremes. Here are found the alcohols, esters, ethers, acids, amines, nitriles, amides, ketones, and aldehydes—to mention a few of the classes of frequent occurrence.

As might be expected, acids and amines generally are more soluble than neutral compounds. The amines probably owe their abnormally high solubility to their tendency to form hydrates, which are more polar than the amines themselves. This explanation is in harmony with the fact that the solubility of amines diminishes as the basicity decreases. It also explains the observation that many tertiary amines are more soluble in cold than in hot water. Apparently at lower temperatures the solubility of the hydrate is involved, whereas at higher temperatures the hydrate is unstable and the solubility measured is that of the free amine.

Monofunctional ethers, esters, ketones, aldehydes, alcohols, nitriles, amides, acids, and amines may be considered together with respect to water solubility. *In most homologous series of this type the upper limit of water solubility will be found in the neighborhood of the member containing five carbon atoms.*

This rule follows from a very general principle, that increased structural similarity between the solute and the solvent is accompanied by increased solubility. Because of the polar nature of water, compounds owe their solubility in it almost entirely to the polar groups which they may contain. As an homologous series is ascended, the hydrocarbon (non-polar) part of the molecule continually increases while the polar function remains essentially

unchanged. There follows, then, a progressive decrease in the solubility in polar solvents such as water.

That the upper limits of water solubility for many series lie in the same neighborhood is due to the fact that the polarities of many functional groups are similar. The particular region (that of the member containing five carbon atoms) in these several series at which the upper limit of water solubility is reached is determined wholly by the altogether arbitrary proportions of solvent and solute chosen for use in this scheme of separation. It would have been equally easy and perhaps as satisfactory to employ a ratio of solute to solvent which would place the limit elsewhere.

The tendency of certain oxygen-containing compounds to form hydrates also contributes to water solubility. The stability of these hydrates is, therefore, a factor in determining water and ether solubility. Such compounds as chloral and pinacol probably owe their great solubility in water to hydrate formation.

The Effect of Chain Branching on Solubility. *A compound having a branched chain is more soluble than the corresponding straight-chain compound.*

This is a very general rule and is particularly useful in connection with simple aliphatic compounds. For example, the solubility of an iso compound differs widely from that of its normal

TABLE XI

	Soluble	Borderline	Insoluble
Acids	Pivalic	Isovaleric	<i>n</i> -Valeric
Acid chlorides	Isobutyryl	<i>n</i> -Butyryl	
Alcohols	Neopentyl	2-Methyl-3-butanol	<i>n</i> -Amyl
Amides	Isobutyramide	<i>n</i> -Butyramide	
Esters	Isopropyl acetate	<i>n</i> -Propyl acetate	
Ketones	Isopropyl methyl	Methyl <i>n</i> -propyl	
Nitriles		Isobutyronitrile	<i>n</i> -Butyronitrile

isomer and is close to that of the next lower normal member of the homologous series in question. Effects of chain branching are shown in Table XI. In general, the more highly branched of two isomeric compounds possesses the greater solubility.

The position of the functional group in the carbon chain also affects solubility. For example, 3-pentanol is more soluble than 2-pentanol, which in turn is more soluble than 1-pentanol. When

the branching effect is combined with moving the functional group toward the center of the molecule, as illustrated by 2-methyl-2-butanol, a very marked increase in solubility is noted. In general, the more compact the structure the greater the solubility, provided that comparisons are made on alcohols of the same type.

Solubility in Ether. Whether a water-soluble compound will dissolve in ether depends on the nature and number of the functional groups. The presence of highly polar groups causes the compound to be very insoluble in ether; salts of amines and of organic acids do not dissolve.

Among non-ionic compounds, those that contain only one functional group are soluble in ether. Compounds containing more than one functional group generally show decreased solubility in ether (and increased solubility in water).

This is a corollary of the generalization concerning the limit of water solubility; for here the hydrocarbon (non-polar) portion of the molecule is kept nearly unchanged and the polar part is multiplied. Ether is essentially a non-polar solvent, approaching the hydrocarbons in its physical properties. Consequently, a change which decreases the ratio of the hydrocarbon portion to the polar portion of the solute will decrease ether solubility. The decrease in solubility in non-polar solvents such as ether is, of course, attended by a corresponding increase in solubility in polar solvents such as water.

In case of doubt concerning solubility or insolubility in ether it is advisable to test the solubility in benzene and classify the compound into S_1 or S_2 as the result of this test. Commercial ether often contains alcohol, which changes its solvent properties considerably.

The Solubility of Solid Compounds in Inert Solvents. Solubility generalizations such as the preceding, based for the most part on structure and molecular weight, are very useful for liquids but cannot be applied with equal success in connection with solid substances.

The dispersion of solute molecules in the solvent is a process resembling to a certain extent the evaporation of a liquid or the melting of a solid. Two of the factors that may be involved in this solution process are *solvation* and *association*.

Studies of solubilities, of properties of solutions, and especially of the melting points of solids indicate that the molecules of cer-

tain solid compounds are held together by intracrystalline forces of considerable magnitude. The existence of these forces is indicated by the fact that a given substance is more soluble in the liquid than in the crystalline state. For example, at 80°, 2.6 g. of dissolved benzoic acid is present in 100 g. of a saturated aqueous solution in contact with solid benzoic acid, whereas a saturated solution at this temperature in contact with liquid benzoic acid contains 7.5 g. of the acid.

Perhaps one of the best indices of the magnitude of these forces in solid compounds is the melting point. A high melting point indicates strong intermolecular forces and consequently a low solubility in inert solvents.¹ The effect of strong intracrystalline forces, indicated by high melting points, is often sufficient to outweigh predictions of solubility based on similarity of structure and composition.

The dicarboxylic acids illustrate the inverse relationship of melting point and solubility. The data in Table XII show that each member with an even number of carbon atoms melts higher

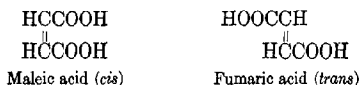
TABLE XII

Even Number of Carbon Atoms		Solubility g./100 g. Water at 20°		Odd Number of Carbon Atoms		Solubility g./100 g. Water at 20°	
	M. P.				M. P.		
Oxalic.....	189°	9.5		Malonic.....	135°	73.5	
Succinic.....	185	6.8		Glutaric.....	97	64	
Adipic.....	153	2		Pimelic.....	103	5	
Suberic.....	140	0.16		Azelaic.....	106	0.24	
Sebacic.....	133	0.10					

than either the immediately preceding or following acid (with an odd number of carbon atoms). The intracrystalline forces in those members with an even number of carbon atoms evidently are greater than in those with an odd number. Since the solubility limit for solids is set at 3.3 g. per 100 ml. of water it is evident that adipic acid (six carbon atoms) is water insoluble but pimelic acid (seven carbon atoms) is water soluble.

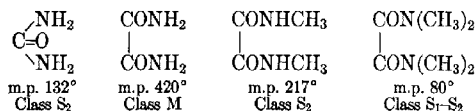
¹ This discussion does not apply to salts; they are highly polar compounds which ionize when dissolved in water and hence are usually very soluble.

The concomitance of high melting point and low solubility is further illustrated by the isomers maleic and fumaric acids.



Fumaric acid sublimates at 200° and is insoluble in water; it is in Class A₁. Maleic acid melts at 130° and is soluble in water. Among *cis-trans* isomers, the *cis* form generally is the more soluble. Similarly, with polymorphous substances such as benzophenone, the lower-melting form possesses the higher solubility.

The diamides of dicarboxylic acids constitute another group of compounds in which the melting point is a valuable index of the forces present in the crystals. Urea, m.p. 132°, is water soluble and is in Class S₂. On the other hand, oxamide has the very high melting point of 420° and consequently a low solubility in water;

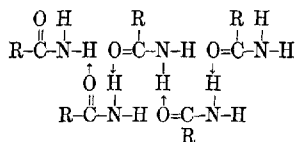


it is in Class M. Substitution of methyl groups for the hydrogen atoms in the amide group lowers the melting point and increases the solubility in water; *N,N'*-dimethyl- and *N,N,N',N'*-tetramethyloxamide are water soluble. Adipamide is water insoluble (Class M), whereas its *N,N,N',N'*-tetraethyl derivative is water soluble.

Amides of the type RCONH₂ and RCONHR obey the general rule that the borderline compounds contain about five carbon atoms. However, *N,N*-dialkylamides (RCONR₂) melt lower than the corresponding unsubstituted amides and are much more soluble in water, the solubility limit being in the neighborhood of nine to ten carbon atoms. It has been suggested that amides having the group -CONH₂ are associated¹ owing to the fact

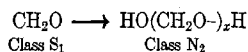
¹ Chaplin and Hunter, *J. Chem. Soc.*, **1937**, 1114; **1938**, 375, 1034; Copley, Zellhoefer, and Marvel, *J. Am. Chem. Soc.*, **60**, 2666 (1938).

that they may act both as acceptors and donors in forming hydrogen bonds.

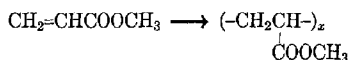


Such an association is not possible for the *N,N*-disubstituted amides (RCONR_2), and hence their state of molecular aggregation is low as indicated by their low melting points and higher solubilities.

Polymers and other compounds of high molecular weight generally exhibit low solubilities in water and ether. Thus formaldehyde is readily soluble in water, whereas paraformaldehyde is insoluble.



Methyl acrylate is soluble in water, but its polymer is insoluble.



Glucose is soluble in water but its polymers—starch, glycogen, and cellulose—are insoluble. Many amino acids are soluble in water, but their condensation polymers, the proteins, are insoluble. The tendency of some types such as proteins, dextrans, and starches to form colloidal dispersions may be deceptive.

Solubility in Dilute Hydrochloric Acid. Aliphatic amines, primary, secondary, and tertiary, form salts (polar compounds) with hydrochloric acid. Hence aliphatic amines are readily soluble in dilute hydrochloric acid.

Aryl groups diminish the basicity of the nitrogen atom; primary aromatic amines, although more weakly basic than primary aliphatic amines, are in Class B; diarylamines and triarylamines are not soluble in dilute hydrochloric acid. Diphenylamine, triphenylamine, and carbazole, for example, are in Class M and not in Class B. Arylalkylamines containing not more than one aryl group are in Class B.

Disubstituted amides ($RCONR_2$) which are of sufficiently high molecular weight to be water insoluble are in Class B, being soluble in dilute hydrochloric acid. This behavior contrasts with that of the simple amides ($RCONH_2$), which are neutral compounds in Class M. Most monosubstituted amides ($RCONHR$) also are neutral and belong in Class M unless they are derived from a very basic amine such as benzylamine. Thus *N*-benzylacetamide is in Class B, whereas acetanilide is in Class M.

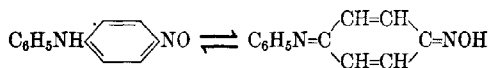
A few types of oxygen-containing compounds that form oxonium salts upon treatment with hydrochloric acid also are in Class B.

Solubility in Dilute Sodium Hydroxide Solutions and in Dilute Solutions of Sodium Bicarbonate. Carboxylic acids, sulfonic acids, sulfinic acids, phenols, some enols, imides, primary and secondary nitro compounds, arylsulfonyl derivatives of primary amines, unsubstituted arylsulfonamides, oximes, thiophenols, and many less familiar types of compounds are soluble in dilute sodium hydroxide solutions. Of these only the three first-mentioned groups are soluble in dilute solutions of sodium bicarbonate.

Negatively substituted phenols such as picric acid, 2,4,6-tribromophenol, and 2,4-dinitrophenol are strongly acidic and are in Class A_1 . Such phenols can be titrated with alkali and give satisfactory neutralization equivalents. In general, only those acidic compounds falling in Class A_1 give satisfactory neutralization equivalents.

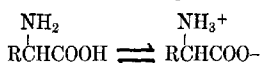
Triacylmethane derivatives such as tribenzoylmethane are highly enolic and are soluble in sodium hydroxide solution. Enolic compounds that are fairly soluble in water but not sufficiently so to be in Class S_1 will often be found in Class A_2 . Apparently their weakly acidic property enhances their tendency to dissolve in water and so renders them soluble in alkali.

Many compounds carrying a hydroxyl group on a nitrogen atom are sufficiently acidic to be in Class A_2 . Oximes illustrate this type. Primary and secondary nitro compounds and imides also belong in this category; their *aci*-forms only are alkali soluble. An interesting example of this is *p*-nitrosodiphenylamine the *aci*-form of which is the isomeric oxime.



Certain of the sodium salts of highly substituted phenols are insoluble in sodium hydroxide. This property may be detected by trying the solubility of any residue in water. Certain phenols which are very insoluble in water may precipitate owing to hydrolysis and hence appear to be insoluble in alkali.

Amphoteric Compounds. Compounds containing both an acidic and a basic group are amphoteric. Low-molecular-weight amino acids exist to some extent as dipolar salts.



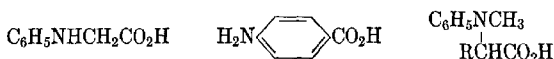
They are soluble in water but not in ether and are in Class S_2 .

The water-insoluble amphoteric compounds are placed in Class $A_1(B)$ or $A_2(B)$, depending on the relative basicity of the amino group, since the basicity determines the extent to which the acidic group will be neutralized by inner salt formation. If the amino group carries only aliphatic substituents, the compounds will dissolve in hydrochloric acid and sodium hydroxide but not in sodium bicarbonate. Compounds of the following types illustrate this group.



They fall in Class $A_2(B)$.

The presence of an aryl group on the nitrogen atom, however, diminishes its basicity so that such compounds fall in Class $A_1(B)$. This is illustrated by the following compounds.



If two aryl groups are attached to the nitrogen atom the compound is not amphoteric and belongs in Class A_1 .



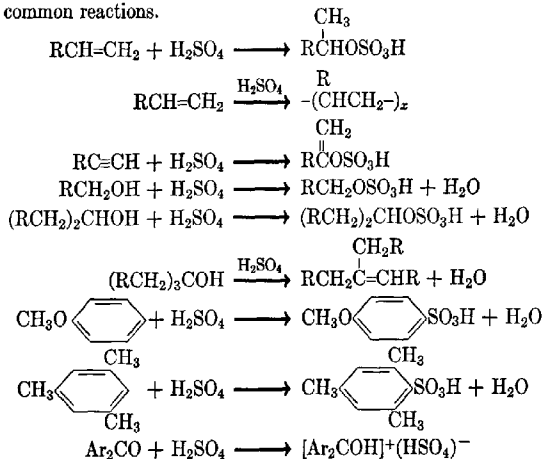
Many other amphoteric compounds in Class $A_2(B)$ are known. These contain basic amino groups as well as the weakly acidic groups characteristic of Class A_2 compounds. Examples are the water-insoluble aminophenols, aminothiophenols, and aminosulfonamides.

Solubility in Syrupy Phosphoric Acid. Alcohols, aldehydes, methyl ketones, cyclic ketones, and esters dissolve in 85% phos-

phoric acid provided that they contain fewer than nine carbon atoms. For ethers the solubility limit appears to be somewhat lower than this. Thus ethyl ether dissolves in 85% phosphoric acid whereas *n*-butyl ether and anisole do not. Some olefins such as amylene are soluble. Ethyl benzoate is insoluble. Certain compounds such as acetophenone and ethyl oxalate form solids with phosphoric acid.

This solvent is particularly interesting because it dissolves compounds without the production of appreciable heat or color—features which frequently are encountered with cold, concentrated sulfuric acid.

Solubility in Cold Concentrated Sulfuric Acid. This solvent is used with neutral, water-insoluble compounds which do not belong in Class M. If the compound is unsaturated, is readily sulfonated, or possesses a functional group containing oxygen, it will dissolve in cold concentrated sulfuric acid. Solution in sulfuric acid frequently is accompanied by reactions such as sulfonation, polymerization, dehydration, or addition of the sulfuric acid to olefinic or acetylenic linkages; but in many cases addition complexes¹ are produced from which the solute may be recovered by dilution with ice water. The following illustrate some of the more common reactions.



¹ Hammett, *Physical Organic Chemistry*, pp. 45 ff., McGraw-Hill Book Co. New York, 1940.

Paraffins, cycloparaffins, and their halogen derivatives are insoluble in sulfuric acid and belong in Class I. Simple aromatic hydrocarbons and their halogen derivatives do not undergo sulfonation under these conditions and are insoluble. However, the insertion of two or more alkyl groups in the benzene nucleus permits the compound to be sulfonated easily, and hence polyalkylbenzenes dissolve rather readily in sulfuric acid. For this reason isodurene and mesitylene fall in Class N₂.

Occasionally the solute may react in such a manner as to yield an insoluble product. All such compounds are considered to be soluble in the reagent and are placed in Class N₁ or Class N₂.

A few high-molecular-weight ethers such as phenyl ether undergo sulfonation so slowly at room temperature that they may not dissolve.

The Relation of Molecular Weight to Solubility. The general effect of increasing the molecular weight by addition of methylene groups in building up an homologous series has been pointed out. As the hydrocarbon part of the molecule increases, the properties of the compounds approach those of the hydrocarbons from which the compounds may be considered to be derived. This means that water solubility decreases and ether solubility increases. A similar change in solubility occurs as the number of aromatic hydrocarbon residues in the molecule increases. Thus α -naphthol and *p*-hydroxybiphenyl are less soluble than phenol. The phenyl radical when present as a substituent in aliphatic acids, alcohols, aldehydes, and similar compounds has an effect on solubility approximately equivalent to a four-carbon-atom aliphatic radical. Benzyl alcohol, for example, is about as soluble as normal amyl alcohol, and hydrocinnamic acid exhibits a solubility similar to that of *n*-heptoic acid.

Another method of increasing the molecular weight of a molecule is by the introduction of halogens. Usually this introduction merely results in a decreased water solubility with the result that some compounds in Classes S₁ and S₂ when substituted by halogens then fall in one of the water-insoluble classes. Increasing the number of halogen atoms also decreases ether solubility but not sufficiently to change the solubility classification.

In certain types of compounds the introduction of halogens may cause changes in the properties of the compound which may outweigh entirely any effect due to molecular weight. For example, trichloroacetic acid is water soluble although its molecular

TABLE XIII
SHOWING THE POSITION OF THE PRINCIPAL BORDERLINES

Compound	Solu- bility Class	Compound	Solu- bility Class
Acids		Esters	
Chloroacetic.....	S ₁	Ethyl acetate.....	S ₁
<i>n</i> -Butyric.....	S ₁	Methyl propionate.....	S ₁
α -Chloropropionic.....	S ₁	<i>n</i> -Propyl formate.....	S ₁
Crotonic.....	S ₁	Isopropyl acetate.....	S ₁
Isovaleric.....	S ₁ -A ₁	<i>n</i> -Propyl acetate.....	S ₁ -N ₁
Valeric.....	A ₁	Methyl isobutyrate.....	S ₁ -N ₁
Alcohols		<i>n</i> -Butyl formate.....	S ₁ -N ₁
<i>n</i> -Butyl.....	S ₁	Methyl isovalerate.....	N ₁
<i>t</i> -Amyl.....	S ₁	<i>sec</i> -Butyl acetate.....	N ₁
Isopropylmethylcarbinol..	S ₁ -N ₁	<i>n</i> -Butyl acetate.....	N ₁
Isoamyl.....	S ₁ -N ₁	Benzyl acetate.....	N ₁
Benzyl.....	N ₁	Ethyl caprylate.....	N ₂
Cyclopentanol.....	N ₁	Ethyl benzoate.....	N ₂
Aldehydes		Methyl carbonate.....	S ₁ -N ₁
Isobutyraldehyde.....	S ₁	Ethyl oxalate.....	S ₁ -N ₁
<i>n</i> -Butyraldehyde.....	S ₁ -N ₁	Methyl malonate.....	S ₁ -N ₁
Isovaleraldehyde.....	N ₁	Ethyl carbonate.....	S ₁ -N ₁
Amides		Ethyl succinate.....	N ₁
Formamide.....	S ₁ -S ₂	Ethyl phthalate.....	N ₁
Acetamide.....	S ₁ -S ₂	Ethyl malonate.....	N ₂
Propionamide.....	S ₁ -S ₂	<i>n</i> -Butyl carbonate.....	N ₁ -N ₂
Isobutyramide.....	S ₁	<i>n</i> -Butyl oxalate.....	N ₂
<i>n</i> -Butyramide.....	S ₁ -M	Ethers	
Formanilide.....	S ₁ -M	Ethyl methyl.....	S ₁
Acetanilide.....	M	Ethyl.....	S ₁ -N ₁
Amines		Ethyl isopropyl.....	S ₁ -N ₁
Diethyl.....	S ₁	Isopropyl.....	N ₁
Isoamyl.....	S ₁	<i>n</i> -Butyl.....	N ₂
<i>n</i> -Amyl.....	S ₁	Hydrocarbons (aromatic)	
Benzyl.....	S ₁	Mesitylene.....	N ₂
Piperidine.....	S ₁	Isodurene.....	N ₂
Cyclohexyl.....	S ₁	Cymene.....	I
Di- <i>n</i> -propyl.....	S ₁ -B	<i>p</i> -Xylene.....	N ₂ -I
Di- <i>n</i> -butyl.....	B	Diphenylmethane.....	I
Aniline.....	B	<i>m</i> -Xylene.....	N ₂ -I
Tri- <i>n</i> -propyl.....	B	<i>o</i> -Xylene.....	N ₂ -I

TABLE XIII—(Continued)
SHOWING THE POSITION OF THE PRINCIPAL BORDERLINES

Compound	Solubility Class	Compound	Solubility Class
Hydrocarbons (aromatic) (Continued)		Nitriles	
Naphthalene.....	I	Propionitrile.....	S ₁
Ketones		Isobutyronitrile.....	S ₁ -M
Ethyl methyl	S ₁	Succinonitrile.....	S ₁ -S ₂ -M
Isopropyl methyl.....	S ₁	Trimethylene cyanide.....	S ₂ -M
Methyl <i>n</i> -propyl.....	S ₁ -N ₁	<i>n</i> -Butyronitrile.....	M
Pinacolone.....	S ₁ -N ₁	Nitro compounds	
Diethyl.....	S ₁ -N ₁	Nitromethane.....	S ₁ -A ₂
Cyclopentanone.....	N ₁	Nitroethane.....	A ₂
Cyclohexanone.....	S ₁ -N ₁	Nitrobenzene.....	M
Acetophenone.....	N ₁	Phenols	
Di- <i>n</i> -butyl.....	N ₁ -N ₂	Hydroquinone.....	S ₁
Benzil.....	N ₂	Chlorohydroquinone.....	S ₁ -A ₂
Benzophenone.....	N ₂	Phloroglucinol.....	S ₂ -A ₂
		Phenol.....	S ₁ -A ₂

weight is near that of nonanoic acid. This introduction of halogens into acetic acid increases the strength of the compound as an acid, trichloroacetic acid being a strong acid.

A similar effect is produced by the halogenation of aniline; the basicity of the amino group is diminished by nuclear halogen atoms. 2,4,6-Tribromoaniline, for example, is not soluble in dilute hydrochloric acid and is in Class M.

BORDERLINES BETWEEN SOLUBILITY CLASSES

In Table XIII are listed a number of compounds selected in such a way as to show the position of the most important of the various borderlines between solubility classes. These compounds have been grouped as far as possible according to chemical nature. In each group an attempt has been made to include the borderline members together with one or more members at either side of the borderlines. The solubility class of a compound not listed

will be evident by considering its relation to the borderline members of the series to which it belongs. Thus the table shows *n*-butyl alcohol to be in Class S_1 ; it follows that the other butyl alcohols and all lower homologs are in this class also. Similarly, since isoamyl alcohol is in Class N_1 it follows that *n*-amyl alcohol and all higher alcohols are in N_1 or N_2 .

TABLE OF SOLUBILITIES

Although it usually is possible to predict the solubility class of a compound by reference to its structural formula, there are many exceptions. Moreover, it occasionally is difficult to classify a compound even by reference to actual experiment; many compounds, as shown in Table XIII, occupy borderline positions. In Table XIV are listed a number of the more common compounds the solubility classes of which are difficult to predict.

TABLE XIV

Compound	Class	Compound	Class
Acetal.....	S ₁ -N ₁	<i>n</i> -Butyl formate.....	S ₁ -N ₁
Acetamide.....	S ₁ -S ₂	<i>n</i> -Butyl mercaptan.....	M
Acetophenone.....	N ₁	<i>n</i> -Butyl oxalate.....	N ₂
Acetoxime.....	S ₁	<i>n</i> -Butyraldehyde.....	S ₁ -N ₁
Acetylpyridine.....	S ₁	<i>n</i> -Butyramide.....	S ₁
Adipic acid.....	A ₁	<i>n</i> -Butyric acid.....	S ₁
Allyl acetate.....	S ₁ -N ₁	<i>n</i> -Butyronitrile.....	M
Allyl alcohol.....	S ₁	<i>n</i> -Butyryl chloride.....	S ₁ -N ₁
β -Aminoethyl alcohol.....	S ₂	Camphor.....	N ₂
α -Aminoisobutyric acid.....	S ₂	Carbon disulfide.....	M
<i>o</i> -Aminophenol.....	S ₁ -S ₂ -A ₂	Catechol.....	S ₁
<i>m</i> -Aminophenol.....	S ₁ -S ₂ -A ₂	Chloral.....	S ₁
<i>p</i> -Aminophenol.....	A ₂	β -Chloroethyl acetate.....	N ₁
α -Amino- <i>n</i> -valeric acid.....	A ₂ (B)	Chlorohydroquinone.....	S ₁ -A ₂
<i>n</i> -Amyl alcohol.....	N ₁	α -Chloropropionic acid.....	S ₁
<i>sec</i> -Amyl alcohol.....	S ₁ -N ₁	Citric acid.....	S ₂
<i>tert</i> -Amyl alcohol.....	S ₁	Cyanoacetic acid.....	S ₁
<i>n</i> -Amylamine.....	S ₁	Cyclohexanol.....	N ₁
Aniline.....	B	Cyclohexanone.....	S ₁ -N ₁
Anthranilic acid.....	A ₁ (B)	Cyclohexyl acetate.....	N ₂
Azelaic acid.....	A ₁	Cyclohexylamine.....	S ₁
Barbituric acid.....	A ₁	Cyclopentanol.....	N ₁
Benzenesulfinic acid.....	S ₁ -A ₁	Cymene.....	I
Benzenesulfonic acid.....	S ₂	Diacetone alcohol.....	S ₁
Benzidine.....	B	Dibenzoylmethane.....	N ₂
Benzoic anhydride.....	N ₂	α,β -Dibromopropionic acid.....	S ₁ -A ₁
Benzoquinone.....	S ₁ -N ₂	2,5-Dichlorohydroquinone.....	A ₂
Benzoylacetone.....	N ₂	α,α' -Dichloromethyl ether.....	S ₁
Benzoylcarbinol.....	S ₁	2,6-Dichloro-4-nitroaniline.....	M
Benzyl alcohol.....	N ₁	Diethylamine.....	S ₁
Benzylamine.....	S ₁	β -Diethylaminoethyl alcohol.....	S ₁
Benzylmalonic acid.....	S ₁ -A ₁	Diethylbarbituric acid.....	A ₂
Benzyl salicylate.....	A ₂	Diethyl ketone.....	S ₁ -N ₁
Biuret.....	S ₂ -M	Dimethyl acetal.....	S ₁ -N ₁
Bromal.....	S ₁	2,4-Dinitroaniline.....	B-M
α -Bromopropionic acid.....	S ₁ -A ₁	Dioxane.....	S ₁
<i>n</i> -Butyl acetate.....	N ₁	Diphenylmethane.....	N ₂ -I
<i>sec</i> -Butyl acetate.....	N ₁	Di- <i>n</i> -propylamine.....	S ₁ -B
<i>n</i> -Butyl alcohol.....	S ₁	Durene.....	N ₂
<i>n</i> -Butyl carbonate.....	N ₁ -N ₂	Ethyl acetate.....	S ₁
<i>n</i> -Butyl ether.....	N ₂		

TABLE XIV—(Continued)

Compound	Class	Compound	Class
Ethyl acetoacetate.....	S ₁	Isopropyl methyl ketone..	S ₁
Ethylal.....	S ₁ -N ₁	Isovaleraldehyde.....	N ₁
Ethyl benzoate.....	N ₂	Isovaleric acid.....	S ₁ -A ₁
Ethyl carbonate.....	S ₁ -N ₁	Isovaleryl chloride.....	S ₁ -N ₁
Ethylenediamine.....	S ₂	Lactic acid.....	S ₂
Ethylene glycol.....	S ₂	Maleic acid.....	S ₁ -S ₂
Ethyl ether.....	S ₁ -N ₁	Malonic acid.....	S ₁
Ethyl lactate.....	S ₁ -N ₁	Mandelic acid.....	S ₁
Ethyl malonate.....	N ₂	Mesitylene.....	N ₂
Ethyl mercaptan.....	S ₁ -M	Mesityl oxide.....	N ₁
Ethyl methyl ether.....	S ₁	N-Methylacetanilide.....	B-M
Ethyl methyl ketone.....	S ₁	Methyl acetoacetate.....	S ₁
Ethyl nitrate.....	S ₁ -M	Methylal.....	S ₁ -N ₁
Ethyl orthoformate.....	S ₁ -N ₁	N-Methylbenzylamine.....	B
Ethyl oxalate.....	S ₁ -N ₁	Methyl n-butyrate.....	S ₁ -N ₁
Ethyl phthalate.....	N ₁	Methyl carbonate.....	S ₁ -N ₁
Ethyl salicylate.....	A ₂	Methyl chloroacetate.....	S ₁ -N ₁
Ethyl succinate.....	N ₁	Methyl citrate.....	S ₁ -N ₁
Formamide.....	S ₁ -S ₂	Methyl isobutyrate.....	S ₁ -N ₁
Formanilide.....	S ₁ -M	Methyl isovalerate.....	N ₁
Fumaric acid.....	A ₁	Methyl levulinate.....	S ₁ -N ₁
Furfuryl alcohol.....	S ₁	Methyl malonate.....	S ₁ -N ₁
Glutaric acid.....	S ₂	Methyl nitrate.....	S ₁ -M
Glycerol.....	S ₂	Methyl orthoformate.....	S ₁ -N ₁
Glycine.....	S ₂	Methyl propionate.....	S ₁
Guanidine.....	S ₂	Methyl-n-propylcarbinol..	N ₁
Hydroquinone.....	S ₁	Methyl n-propyl ketone.....	S ₁ -N ₁
p-Hydroxybenzaldehyde....	A ₂ -N ₁	o-Nitroaniline.....	B-M
o-Hydroxybenzyl alcohol..	S ₁ -A ₂	m-Nitroaniline.....	B
Indene.....	N ₂	p-Nitroaniline.....	B
Indole.....	M	Nitroguanidine.....	A ₂ -M
Isoamyl alcohol.....	S ₁ -N ₁	Nitromethane.....	S ₁ -A ₂
Isoamylamine.....	S ₁	p-Nitrosodiphenylamine....	A ₂ -M
Isoamyl salicylate.....	A ₂ -N ₂	Nitrourea.....	A ₂ -M
Isobutyl formate.....	S ₁	Oxamide.....	M
Isobutyraldehyde.....	S ₁	Paraldehyde.....	S ₁ -N ₁
Isobutyramide.....	S ₁	Phenol.....	S ₁ -A ₂
Isobutyronitrile.....	S ₁ -M	Phenoxyacetic acid.....	S ₁ -A ₁
Isobutyryl chloride.....	S ₁	o-Phenylenediamine.....	S ₁ -S ₂
Isodurene.....	N ₂	m-Phenylenediamine.....	S ₁ -S ₂
Isopropyl acetate.....	S ₁	p-Phenylenediamine.....	S ₂

TABLE XIV—(Continued)

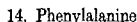
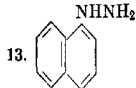
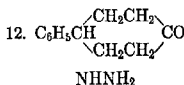
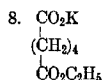
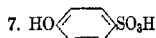
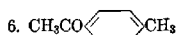
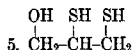
Compound	Class	Compound	Class
Phenylhydrazine.....	B	Sebacic acid.....	A ₁
Phloroglucinol.....	S ₂ -A ₂	Succinic acid.....	S ₁ -S ₂
Phthalic acid.....	A ₁	Succinimide.....	S ₁ -S ₂
Phthalic anhydride.....	N ₁	Succinonitrile.....	S ₁ -S ₂ -M
Phthalimide.....	A ₂	Sulfanilic acid.....	A ₁
Picric acid.....	A ₁	Triacetin.....	S ₁ -N ₁
Pimelic acid.....	S ₁ -A ₁	2,4,6-Tribromoaniline.....	M
Pinacol.....	S ₁	2,4,6-Tribromophenol.....	A ₁
Piperidine.....	S ₁	2,4,6-Trichloroaniline.....	B-M
Polyoxymethylene.....	S ₂ -N ₂	2,4,6-Trichlorophenol.....	A ₁
Propionamide.....	S ₁ -S ₂	Trimethylene cyanide.....	S ₂ -M
Propionitrile.....	S ₁	Trimethylene glycol.....	S ₂
Propionyl chloride.....	S ₁	α -Triphenylguanidine.....	B-M
<i>n</i> -Propyl acetate.....	S ₁ -N ₁	Tri- <i>n</i> -propylamine.....	B
Propylene glycol.....	S ₁	Urea.....	S ₂
<i>n</i> -Propyl formate.....	S ₁	<i>n</i> -Valeraldehyde.....	N ₁
Protocatechualdehyde.....	S ₁ -A ₂	<i>n</i> -Valeric acid.....	A ₁
Pyridine.....	S ₁	Vanillin.....	A ₁
Pyrrrole.....	M	Xylenes.....	N ₂ -I
Resorcinol.....	S ₁		

EXERCISES

I. Tabulate as shown in the illustrative table the formulas, names, and solubility classes of the following compounds.

Structural Formula	Distinctive Common and/or Systematic Names	Solubility Class	Reasons for the Solubility Classification
$\begin{array}{c} \text{NH}_2 \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{Cl} \end{array}$	<i>p</i> -Chloroaniline	B	Insoluble in water because it has six carbon atoms and a chlorine atom. It is basic, only one aryl group being attached to the amino group.
$\text{CH}_3\text{CO}(\text{CH}_2)_4\text{CH}_3$	2-Heptanone	N ₁	A methyl ketone with more than five but fewer than nine carbon atoms.

1. *n*-Butyl chloride2. $\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{NH}_2$ 3. $\text{C}_6\text{H}_5\text{CH}=\text{CH}\text{C}_6\text{H}_4\text{OH}$ 4. $(\text{CH}_3)_2\text{CHNHCH}_3$

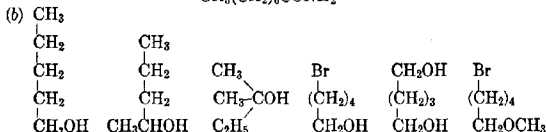
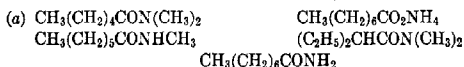


II. (a) Arrange the following compounds in the approximate order of their basicity toward dilute aqueous hydrochloric acid.

1. Benzanilide.
2. *n*-Amylamine.
3. Diphenylamine.
4. 2,6-Dibromo-4-methylaniline.
5. Benzylamine.
6. *o*-Bromoaniline.
7. *p*-Toluidine.

(b) Which of the above compounds would fall in Class B? Class M? Class S₁?

III. Arrange the following compounds in the order of increasing solubility in water. Give reasons for the arrangement.



IV. Group the following compounds in the approximate order of decreasing acidity, and state the solubility class of each.

1. *meso*-Tartaric acid.
2. Stearamide.
3. *p*-Toluenesulfonic acid.
4. 2-Bromo-6-nitrophenol.
5. Saccharin.
6. α -Naphthoic acid.
7. β -Naphthol.
8. Benzohydroxamic acid.
9. *p*-Toluenesulfonamide.
10. Desoxybenzoin.
11. *p*-Thiocresol.
12. Ethyl α -benzoylacetoacetate.

CHAPTER VII

APPLICATION OF CLASSIFICATION TESTS

In the examination of an organic compound, the use of classification tests follows the determination of the boiling point (or melting point), solubility, and behavior on ignition. From these data and the appearance of the compound (color, physical state, odor), it is possible to place the compound in one or two solubility classes. Moreover, these experiments serve to uncover clues as to the type of functional groups that may be present. The next step in the identification is to seek specific information concerning the presence or absence of common functional groups. For this purpose, a number of classification reagents must be selected not only to provide positive indications of the presence of a functional group but also to exclude many classes of compounds as well.

In each of the experiments included in this chapter, directions are given for the use of a reagent which has been found to be useful in the detection of functional groups. Few of these reagents are specific for a particular functional group, since each of the tests possesses certain limitations. Consequently, it usually is necessary to try several of them before a satisfactory classification can be made. However, it is unnecessary to try all the reagents on each unknown. Such a mode of attack not only wastes time but may actually be dangerous.

The following suggestions offer a means of initiating the attack on the problem of establishing or excluding the presence of functional groups. At the same time that a test is applied to an unknown compound, a control test should be carried out on the known compounds suggested in each experiment. Thus, it is possible to make direct and immediate comparisons between the results of the experiments on the known and unknown compounds. It is very important to observe just what positive and negative tests look like.

Selection of Classification Tests

For ready reference the classification tests have been arranged alphabetically in the form of numbered experiments. In the following discussion the numbers in parentheses refer to these experiments.

Unsaturation. The tests for double or triple bonds (5, 24) should be applied to compounds in all solubility classes except those in Class I.

Halogen Compounds. Both the alcoholic silver nitrate (25) and the sodium iodide (30) tests should be tried in order to obtain information concerning the reactivity of the halogen.

Class S₁ Compounds Containing No Nitrogen and Neutral to Litmus; Class N₁-N₂ Compounds. Alcohols may be detected by means of acetyl chloride (1*d*), benzoyl chloride (1*e*), or sodium (26). If these tests are positive, further information may be obtained by applying the Lucas test (15), periodic acid (22), the iodoform test (29), ceric nitrate (7), or iodic acid (17). Ethers may be cleaved with hydriodic acid (14) and, if aromatic, will undergo bromination slowly (5). The carbonyl group in aldehydes and ketones responds to tests with hydroxylamine (16), phenylhydrazine (23), and 2,4-dinitrophenylhydrazine (8). Further differentiation results from the use of fuchsin (13), Benedict's solution (3), Tollens' reagent (33), mercuric chloride-sodium ethoxide (18), or sodium hypoiodite (29). Esters are hydrolyzed by sodium hydroxide solution (28*b*) and give useful saponification equivalents (28*b*). Anhydrides and acyl halides react with aniline to give anilides (1*b*, 1*e*) and are hydrolyzed by alkali (28*b*). The acid which is produced may be characterized by reference to the neutralization equivalent (28*a*), the partition coefficient (35), or the Duclaux constants (34). Hydrocarbons in classes N₁ and N₂ may be distinguished from compounds having oxygen-containing functional groups by means of the ferrox test (11).

Class S₁ Compounds Acidic to Litmus and Containing No Nitrogen. Low-molecular-weight acids may be characterized by means of their water-ether partition coefficients (35), Duclaux constants (34), or neutralization equivalents (28*a*). Low-molecular-weight acid chlorides and anhydrides may be hydrolyzed to the corresponding acids (1*a*) or converted to anilides (1*b*). Occasionally it may be necessary to apply tests for hydroxyl (1*d*, 1*e*) or carbonyl groups (23).

Class S₁ and S₂ Compounds Containing Nitrogen and Basic to Litmus; Class B Compounds. Basic primary, secondary, and tertiary amines are found in these solubility classes and are detected by means of the Hinsberg test (4), nitrous acid (21), the nickel chloride-5-nitrosalicylaldehyde complex (20), or by formation of the nickel salt of a dialkylaminodithiocarbamate (19). Aryl-amines also undergo bromination readily (6). Class S₂ and Class B amines may contain functional groups (such as hydroxyl, carbonyl, cyano, nitro) in addition to the basic amino groups. Hence tests for these groups should be applied when necessary.

Class S₂ Compounds

- (a) *Salts of Carboxylic Acids.* A solution of the salt is acidified and the free carboxylic acid liberated. If the acid is water insoluble, it is removed by filtration and treated as a Class A₁ compound. If the acid is soluble in the aqueous solution, it may be isolated by extraction with ether or chloroform and subsequent removal of the solvent by distillation.
- (b) *Salts of Sulfonic Acids.* A salt of a sulfonic acid is best converted to the corresponding chloride by treatment with phosphorus pentachloride. The sulfonyl chloride yields a sulfonamide when treated with ammonium hydroxide. When the amide has been purified and its melting point has been determined, a list of possible compounds may be made (see p. 273).
- (c) *Salts of Amines.* Addition of alkali will liberate the free bases, which, depending on their solubilities, can be assigned to Class S₁, Class S₂, or Class B and treated accordingly. Usually it is time-saving and more convenient to apply the various tests for amines (1b, 4, 21, 20, 19, 6) directly on the amine salt.
- (d) *Polyfunctional Compounds.* Polybasic acids and hydroxy acids are best characterized by reference to their neutralization equivalents (28a). The sugars, which give a characteristic charring and a caramel odor in the ignition test, should be treated with Benedict's solution (3) and Tollens' reagent (33). If a reducing sugar is present, the osazone test (23) is applied. If no reduction occurs, the unknown should be boiled for a few minutes with dilute

hydrochloric acid and the tests repeated. If a positive test for a sugar is obtained, the optical rotation should be determined (p. 47). Polyatomic alcohols and keto alcohols in Class S_2 are detected by reaction with acid halides (1), hydroxylamine (16), phenylhydrazine (23), 2,4-dinitrophenylhydrazine, or periodic acid (22). Some amino acids may fall in Class S_2 as well as in Class A_1 -B, or Class A_2 -B. These may be tested with nitrous acid (21). Neutralization equivalents (28a) of the benzoyl derivatives (1e) may be determined also.

Class A_1 Compounds. Both the carboxylic and sulfonic acids give satisfactory neutralization equivalents (28a). Hydroxy acids react with acetyl chloride (1d). Phenolic acids give positive tests with bromine water (6) and ferric chloride (10). Carbonyl groups in these acids are best detected by phenylhydrazine (23). If nitrogen is present, treatment with hot sodium hydroxide solution (28d) will liberate ammonia from cyano groups and ammonia or amines from amido groups. The zinc-ammonium chloride reagent (36) or ferrous hydroxide test (12) is used to detect nitro groups.

Class A_2 Compounds. Phenols are the commonest type of compounds in this class. They are indicated by the acetyl chloride test (1d), bromine water (6), ceric nitrate (7), iodic acid (17), and nitrous acid (21e) as well as reduction of permanganate (24). Phenols must be tested also for other functional groups such as cyano (28d), keto (23), and nitro (12, 36).

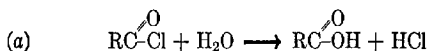
Class M Compounds. Hydrolysis with hot sodium hydroxide solution (28d) is used to convert amides, substituted amides, nitriles, and certain negatively substituted aromatic amines to the corresponding acids or phenols with liberation of ammonia or amines. Nitro groups may be detected by the use of tin and hydrochloric acid (32), ferrous hydroxide (12), or zinc and ammonium chloride (36). Alcoholic groups are tested for with acetyl chloride (1d), and carbonyl groups with hydroxylamine (16) or phenylhydrazine (23). Ester groups are hydrolyzed by alkali (28d).

Class I Compounds. If the compound contains reactive halogen, as indicated by the silver nitrate (25) or the sodium iodide test (30), it must be partly or wholly aliphatic. Fuming sulfuric acid (31) can be used to detect aromatic nuclei whether halogen is present or absent. Condensation with azoxybenzene (2a) or

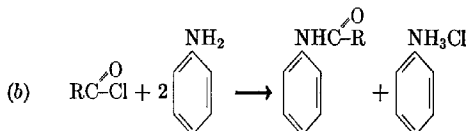
with chloroform (2b) in the presence of aluminum chloride also serves to detect the presence of aromatic rings.

EXPERIMENT 1

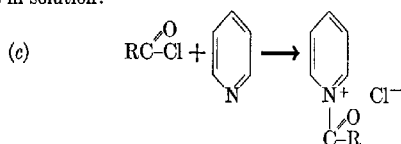
Acid Chlorides



Cautionously add a few drops of acetyl chloride to 1 ml. of water and note what happens. In a similar manner test the behavior of benzoyl chloride towards water.¹ What difference do you observe?



Repeat each of the foregoing tests using 0.5 ml. of aniline in place of water. What are the products of this reaction? Pour the mixture into 5 ml. of water. What is the precipitate? What is in solution?



Treat 0.5 ml. of pyridine or quinoline with a few drops of acetyl chloride. Account for the generation of heat in this reaction notwithstanding the fact that the original is recovered on dilution of the mixture with water followed by neutralization.

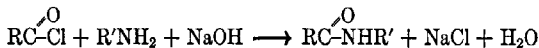
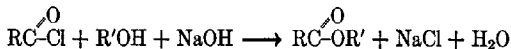


Add drop by drop 1 ml. of acetyl chloride to: (1) 1 ml. of ethanol; (2) 0.5 g. of phenol. In each case allow the reaction mixture to stand for a minute or two and then pour it cautiously into

¹Take care to destroy excess benzoyl chloride with dilute ammonium hydroxide solution before pouring the residues into the sink. This compound is strongly lachrymatory.

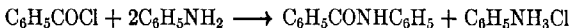
5 ml. of water. In 2, remove the liquid and test its solubility in cold dilute sodium hydroxide solution.

(e) **The Schotten-Baumann Reaction**



In a small glass-stoppered bottle place 5 ml. of ethanol, 10 ml. of water, and 2 ml. of benzoyl chloride. To this solution add in portions, with vigorous shaking, 10 ml. of 20% sodium hydroxide solution. Shake the mixture for several minutes, and then test the solution with litmus paper to make sure that it is still alkaline. What are the products of the reaction? Repeat the above experiment using 2 ml. of aniline instead of the ethanol. What advantage does this procedure possess over benzoylation without the use of alkali as in part *b*? Upon what factors does the success of the Schotten-Baumann reaction depend?

Discussion. Advantage is taken of the reactivity of acid chlorides to prepare acid derivatives, notably esters and amides. Acid chlorides react with alcohols, phenols, and amines to form hydrogen chloride and the ester or amide. This type of reaction is most useful with primary and secondary amines. Thus, benzoyl chloride reacts with aniline to give benzanilide. The hydrogen chloride eliminated is taken up by a second mole of the base.



Acylation takes place less readily with alcohols and phenols, and, as a consequence, alkali is often used to accelerate the reaction since it neutralizes the hydrochloric acid which is eliminated.

Tertiary alcohols react abnormally to give alkyl chlorides.



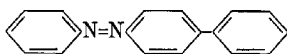
EXPERIMENT 2

Aluminum Chloride with Azoxybenzene or Chloroform

(a) Place 2 ml. of dry benzene in a clean, dry test tube; add one or two crystals of azoxybenzene and about 0.1 g. of anhydrous aluminum chloride. Note the color. If no color is produced im-

mediately, warm the mixture for a few minutes. Try the test on petroleum ether, chlorobenzene, ethyl bromide, and naphthalene.¹

Discussion. This test should be applied only to those compounds whose solubility behavior places them in Class I. The color produced is due to an addition compound formed from *p*-phenylazobenzene and aluminum chloride.²



p-Phenylazobenzene

Aromatic hydrocarbons derived from benzene and their halogen derivatives produce a deep orange to dark red color in solution or give a precipitate. Condensed nuclear hydrocarbons such as naphthalene, anthracene, and phenanthrene produce brown colors. Aliphatic hydrocarbons give no color or, at most, a pale yellow.

(b) To 2 ml. of dry chloroform in a test tube add 0.1 ml. (or 0.1 g.) of benzene. Mix thoroughly, and incline the test tube so as to moisten the wall. Then add 0.5 to 1.0 g. of anhydrous aluminum chloride so that some of the powder strikes the side of the test tube. Note the color of the powder on the side, also the color of the solution. Try the test on petroleum ether, chlorobenzene, and biphenyl.

Discussion. The colors produced by the reaction of aromatic compounds with chloroform and aluminum chloride are quite characteristic. Aliphatic compounds in solubility Class I give no color, or only a very light yellow. Typical colors produced are the following:

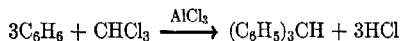
COMPOUND	COLOR
Benzene and its homologs	Orange to red
Aryl halides	Orange to red
Naphthalene	Blue
Biphenyl	Purple
Phenanthrene	Purple
Anthracene	Green

With time the colors change to various shades of brown. Similar colors are obtained when chloroform is replaced by carbon tetrachloride.

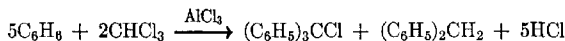
¹ If the hydrocarbon is a solid, a solution of 0.5 g. of it in 2 ml. of dry carbon disulfide may be used.

² See Pummerer and Binapfel, *Ber.*, **54**, 2768 (1921), and Pummerer, Binapfel, Bittner, and Schuegraf, *Ber.*, **55**, 3095 (1922).

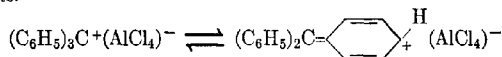
The chief product of the Friedel-Crafts reaction between chloroform and benzene is triphenylmethane.



However, the reaction appears to take place in steps producing some diphenylchloromethane; also, disproportionation occurs so that some triphenylchloromethane is formed.

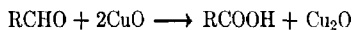


The colored compounds are formed by combination of the organic chloride with aluminum chloride to produce carbonium salts.



EXPERIMENT 3

Benedict's Solution



To a solution of 0.2 g. of glucose in 5 ml. of water add 5 ml. of Benedict's solution and heat the mixture to boiling. Repeat the experiment, using, in place of glucose: (a) sucrose; (b) glycerol; (c) maltose; (d) lactose; (e) phenylhydrazine. Try the test on sucrose (0.2 g.) which has been boiled for a few minutes with 5 ml. of water containing 2 drops of concentrated hydrochloric acid. It is necessary to neutralize the hydrochloric acid before the Benedict's solution is added. Why?

Reagent. Benedict's solution is made by dissolving the following salts in distilled water.

Hydrated copper sulfate (17.3 g.).

Sodium citrate (173.0 g.).

Anhydrous sodium carbonate (100 g.).

The citrate and carbonate are dissolved by heating with 800 ml. of water. Additional water is added to bring the volume of solution to 850 ml. The copper sulfate is dissolved in 100 ml. of water, and the resulting solution is poured slowly, with stirring, into the

solution of citrate and carbonate. The final solution is made up to 1 l. by addition of water.

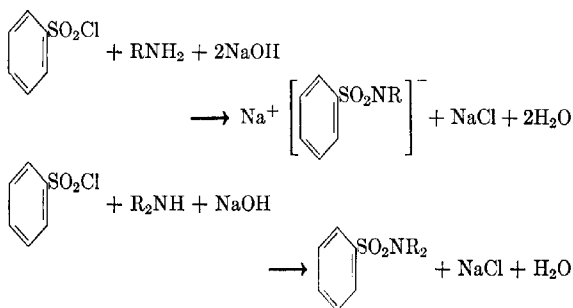
Discussion. Benedict's solution is used widely to test for aliphatic aldehydes and is particularly suitable for the detection of reducing sugars. It is sensitive to 0.01% concentration of glucose. The color of the precipitate may be red, yellow, or green, depending on the amount of reducing agent present.

A method of distinguishing aromatic from aliphatic aldehydes is to use both Benedict's and Tollens' tests. The latter is positive for all aldehydes; the former, only for aliphatic aldehydes.¹

EXPERIMENT 4

Benzenesulfonyl Chloride

Hinsberg's Method for Distinguishing Primary, Secondary, and Tertiary Amines



To 0.3 ml. of aniline in a test tube add 5 ml. of 10% sodium hydroxide solution and 0.4 ml. of benzenesulfonyl chloride. Stopper the test tube, and shake the mixture very vigorously.² Test the solution to make sure that it is alkaline. After all the benzenesulfonyl chloride has reacted, cool the solution and filter or decant from any residue (A). Note whether the residue A is a solid or liquid and whether it is lighter or heavier than the alkaline

¹ Tollens, *Ber.*, **14**, 1950 (1881).

² If the reaction mixture heats up considerably it should be cooled. Certain *N,N*-dialkylanilines produce a purple dye if the mixture becomes too hot. This may be prevented by carrying out the reaction at 15 to 20°.

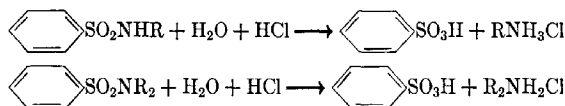
solution. What information can you deduce from these observations? Test the solubility of this residue (A) in water and in dilute hydrochloric acid. Note that solubility of A in hydrochloric acid indicates that the original was a tertiary amine. The sodium salts of certain sulfonamides of high molecular weight may be insoluble in the alkaline solution.¹ Usually they are soluble in water.

Acidify the clear filtrate. Scratch the test tube to hasten crystallization of the product (B).

Repeat this test using methylaniline and dimethylaniline instead of aniline. Some secondary amines react slowly, and it is occasionally necessary to warm the reaction mixture.

Show by means of a diagram how the above procedure distinguishes between primary, secondary, and tertiary amines.

When the Hinsberg method is used to separate mixtures of amines it is necessary to recover the pure individual amines. The benzenesulfonamides may be hydrolyzed as follows.



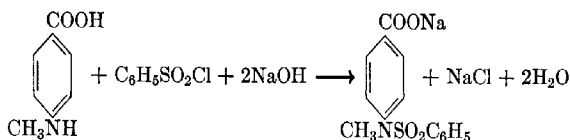
In order to obtain sufficient material, the separation described above is carried out using 50 times the amounts stated.

The individual sulfonamides are then hydrolyzed by refluxing 8 to 10 g. of each with 100 ml. of 25% hydrochloric acid. Sulfonamides of primary amines require 24 to 36 hours' refluxing, whereas sulfonamides of secondary amines may be hydrolyzed in 10 to 12 hours. After solution is complete, the mixture is cooled, made alkaline with 20% sodium hydroxide solution, and extracted with three 50-ml. portions of ether. The ether solution is dried, and, after the ether has been driven off, the amine is distilled. With certain very low- or very high-boiling amines it is often more convenient to recover them as hydrochlorides by passing dry hydrogen chloride gas into the dry ether solution.

Discussion. Arylsulfonyl chlorides are especially useful in characterizing primary and secondary amines. The Hinsberg method

¹ Certain primary amines may yield alkali-insoluble disulfonyl derivatives. These may be hydrolyzed by boiling for 30 minutes with 5% sodium ethoxide in absolute ethanol.

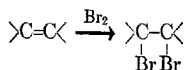
for separating amines is based on the fact that the sulfonamides of primary amines are soluble in alkali, whereas those of secondary amines are not. Since tertiary amines do not give amides, the method provides a means of classifying and separating the three types of amines. However, the results of the Hinsberg test must not be used alone in classifying amines; it is necessary to consider also the solubility of the original compound. If that compound is amphoteric, i.e., soluble in both acids and alkalies, the Hinsberg method fails to distinguish between the classes. For example, *p*-(*N*-methylamino)-benzoic acid reacts with benzenesulfonyl chloride and alkali to give a solution of the sodium salt of the *N*-benzenesulfonyl derivative.



Acidification precipitates the free acid; this fact taken by itself would indicate that the original compound was a primary rather than a secondary amine.

EXPERIMENT 5

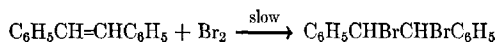
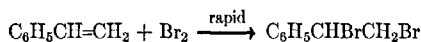
Bromine in Carbon Tetrachloride Solution



In this test 0.1 g. (0.2 ml. of a liquid) of the compound to be tested is added to 2 ml. of carbon tetrachloride, and a 5% solution of bromine in carbon tetrachloride is added drop by drop (with shaking) until the bromine color persists. Apply the test to: (a) 2-pentene; (b) pentane; (c) benzene; (d) phenol; (e) formic acid; (f) benzaldehyde; (g) ethanol; (h) allyl alcohol; (i) acetophenone; (j) aniline.

Discussion. This reagent is widely used to test for the presence of an olefinic or acetylenic linkage. Carbon tetrachloride is a good solvent for bromine and for many organic compounds but does not dissolve hydrogen bromide. The evolution of hydrogen bromide

is, accordingly, accepted as evidence that the reaction is substitution rather than addition. When employed in detecting unsaturation this reagent may lead to erroneous conclusions for two reasons. The first is that not all olefinic compounds take up bromine. The presence of negative groups on the carbon atoms of an ethylenic bond causes the addition to be slow and in extreme cases inhibits the reaction. The following will illustrate this point.



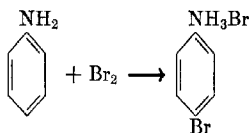
It has been noted also that the rate of reaction of bromine with unsaturated compounds is influenced by the presence of oxygen. Cinnamic acid reacts rather slowly with bromine if the reaction is carried out with the reactants exposed to the air, but the reaction proceeds rapidly if oxygen is excluded.¹ A positive test for unsaturation is one in which the bromine color is discharged *without* the evolution of hydrogen bromide.

Discharge of the bromine color *accompanied by the evolution of hydrogen bromide*, indicating that substitution has occurred, is characteristic of compounds that are readily brominated. In this category are enols, many phenols, and a number of compounds that contain active methylene groups. In testing ketones it is to be noted that the reaction often is slow to start. Methyl ketones appear to be more reactive than other ketones but, like other carbonyl compounds, may exhibit an induction period. Simple esters do not give this test. Ethyl acetoacetate decolorizes the solution immediately while ethyl malonate may require as much as a minute. A number of active methylene compounds that do not discharge the color at room temperature readily give a test at 70°. Among these substances are propionaldehyde and cyclopentanone. Aryl ethers behave similarly. Benzyl cyanide, even at 70°, may require several minutes.

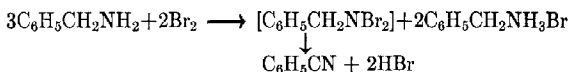
Aromatic amines are exceptional in that the first mole of hydrogen bromide formed is not evolved but reacts to convert the

¹ Bauer and Daniels, *J. Am. Chem. Soc.*, **56**, 2014 (1934).

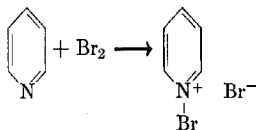
amine to its salt. For this reason the reaction is often mistaken for simple addition.



Benzylamine represents an unusual type which reacts readily with bromine. Substitution of the hydrogen atoms on the nitrogen atom appears to take place followed by decomposition to benzonitrile.



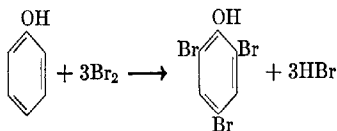
Certain tertiary amines such as pyridine form perbromides upon treatment with bromine.



The bromine color is likewise discharged by aliphatic amines of all types.

EXPERIMENT 6

Bromine Water



Prepare 1% aqueous solutions of (a) phenol, (b) aniline, (c) salicylic acid, and (d) *p*-nitrophenol; to each solution add bromine water drop by drop until the bromine color is no longer discharged.

Discussion. An excess of bromine water converts tribromophenol to a yellow tetrabromo derivative, which may be 2,4,6-tribromophenyl hypobromite or 2,4,4,6-tetrabromocyclohexadienone.¹ The tetrabromo compound is readily converted to the tribromophenol by washing with 2% hydriodic acid.

Why is tribromoaniline insoluble in dilute hydrobromic acid? In what solubility class is it found? Could the decolorization of the bromine water result from the presence of an inorganic compound? Give examples. Is bromine hydrolyzed in water? What effect would bromine water have on a water-soluble salt of a water-insoluble acid?

EXPERIMENT 7

Ceric Nitrate Reagent

(a) **For Water-soluble Compounds.** Dilute 0.5 ml. of the ceric nitrate reagent with 3 ml. of distilled water in a test tube and mix thoroughly. Add 4 to 5 drops of the compound to be tested, shake the mixture, and note the change in color. Try this test on: (a) ethanol; (b) glycerol; (c) tartaric acid; (d) glucose; (e) phenol. If the compound is a solid, dissolve it in water and add 4 to 5 drops of the aqueous solution to the reagent.

(b) **For Water-insoluble Compounds.** To 0.5 ml. of the reagent in a test tube add 3 ml. of dioxane. If a precipitate forms, add water (3 to 4 drops), with shaking, until the solution is clear. Add 4 to 5 drops of the compound to be tested, shake, and note the color. Try the test on: (a) heptyl alcohol; (b) benzyl alcohol; (c) salicylic acid. If the compound is a solid, dissolve it in dioxane and add 4 to 5 drops of the dioxane solution to the reagent.

Reagent. Dissolve 200 g. of ceric ammonium nitrate $[(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6]$ in 500 ml. of 2 *N* nitric acid. The solution process is accelerated greatly by heating.

Discussion. A positive test for an alcohol is indicated by a change in the color of the reagent from yellow to red. Phenols give a brown to green-brown precipitate in aqueous solution; a very deep red to brown coloration is formed in dioxane.

A positive test is obtained with alcohols and phenols containing no more than ten carbon atoms. With larger molecules too little color is given for the test to be useful. Hydroxy acids, hydroxy

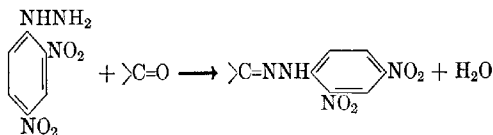
¹ Lauer, *J. Am. Chem. Soc.*, **48**, 442 (1926).

aldehydes, and most other compounds containing an alcoholic hydroxyl group, and coming within the limit described above, give a positive test. Amino alcohols raise the pH to such an extent that the ceric ion precipitates as the hydroxide and the test fails.

Aldehydes, ketones, acids, alkyl halides, esters, and other common compounds containing only carbon, hydrogen, oxygen, and halogen do not interfere. Aromatic amines, amine hydrochlorides, and compounds containing structures commonly oxidized to chromophoric groups give colors or precipitates with the reagent. For this reason aromatic amines sometimes give the phenol test. Compounds which are very rapidly oxidized sometimes decolorize the ceric nitrate solution before the test can be seen.¹

EXPERIMENT 8

2,4-Dinitrophenylhydrazine



To 3 ml. of the 2,4-dinitrophenylhydrazine reagent add 1 or 2 drops of the compound to be tested and shake vigorously. Allow the solution to stand 15 minutes if no precipitate forms immediately. The dinitrophenylhydrazones of all aldehydes and ketones are very insoluble and usually precipitate immediately. The precipitate may be oily at first but on standing becomes crystalline. Try this test on: (1) formalin; (2) acetone; (3) butyraldehyde; (4) benzaldehyde; (5) acetophenone; (6) ethyl acetoacetate.

Reagent. The reagent is prepared by dissolving 2 g. of 2,4-dinitrophenylhydrazine in 15 ml. of concentrated sulfuric acid. This solution is then added, with stirring, to 150 ml. of 95% ethanol, and the solution is diluted to 500 ml. with distilled water. The solution is mixed thoroughly and filtered. Since it is very dilute

¹ Duke and Smith, *Ind. Eng. Chem., Anal. Ed.*, **12**, 201 (1940).

it serves as a qualitative reagent only. In order to obtain sufficient material for use as a derivative follow Procedure 15, page 171.

What is the advantage of this reagent over phenylhydrazine? How is 2,4-dinitrophenylhydrazine prepared? What is formed as the final condensation product of ethyl acetoacetate with: (a) phenylhydrazine? (b) 2,4-dinitrophenylhydrazine?

EXPERIMENT 9

Fehling's Solution



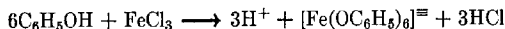
To a solution of 0.2 g. of glucose in 5 ml. of water add 5 ml. of Fehling's solution, and heat the mixture to boiling. Repeat the experiment using in place of glucose: (a) sucrose; (b) glycerol; (c) maltose; (d) lactose; (e) phenylhydrazine. Try the test on sucrose (0.2 g.) which has been boiled for a few minutes with 5 ml. of water containing 2 drops of concentrated hydrochloric acid. It is necessary to neutralize the hydrochloric acid before the Fehling's solution is added. Why? Fehling's solution is prepared by mixing equal volumes of the following solutions just before use.

No. 1. Copper sulfate solution (34.6 g. of hydrated copper sulfate crystals in 500 ml. of water).

No. 2. Sodium potassium tartrate (173 g.) and sodium hydroxide (70 g.) in 500 ml. of water.

EXPERIMENT 10

Ferric Chloride Solution



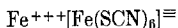
Prepare dilute aqueous solutions (about 0.1%) of (a) phenol, (b) ethyl acetoacetate, (c) resorcinol, (d) benzoic acid, (e) *p*-hydroxybenzoic acid, and (f) salicylic acid; to each solution add a drop of 1% ferric chloride solution. Compare the color produced with that of pure water and a drop of ferric chloride solution. Occasionally the color produced is not permanent; hence care should be taken to watch the solution closely at the instant the drop of ferric chloride is added.

Discussion. The production of a coloration with ferric chloride solution¹ is typical of phenols and enols; but many of them do not give colors, so a negative test must not be taken as significant without supporting evidence. Sometimes it is possible to get a positive test by the use of an alcoholic solution; if the test in aqueous solution is negative it is well to try it in alcoholic solution.

Most oximes also give a red color with ferric chloride solution.

EXPERIMENT 11

Ferric Hexathiocyanatoferrate. Ferrox Test²



Add a small piece (0.5 by 1.0 cm.) of Ferrox test paper to 4 or 5 drops of each of the following substances in a small test tube (8 by 50 mm.): (a) benzene; (b) ethyl ether; (c) ethyl benzoate; (d) mineral oil; (e) cottonseed oil; (f) 2-pentene; (g) mesitylene. Note whether the liquids assume a deep red color.

Reagent. The Ferrox test paper is made by soaking filter paper in a methanol solution of ferric hexathiocyanatoferrate. The latter is prepared by dissolving 1.0 g. of potassium thiocyanate and 1.0 g. of ferric chloride in separate 10-ml. portions of methanol. The solutions are mixed, and the precipitate of potassium chloride is removed by filtration. The filter paper is dipped in the filtrate once or twice, dried, and preserved in brown, stoppered bottles.

Discussion. Compounds containing oxygen dissolve the red complex salt and produce a deep red solution. Alcohols, ethers, esters, aldehydes, ketones, and amides give a positive test. Saturated, unsaturated, and aromatic hydrocarbons as well as their halogen derivatives do not dissolve the salt; their solutions are not colored, and the test is negative. A few high-molecular-weight ethers such as phenyl ether and alkyl β -naphthyl ethers give negative tests. Solid compounds may be tested by dissolving them in benzene or toluene.

It seems probable that the ferric hexathiocyanatoferrate forms a complex with the cellulose, which of course contains oxygen in its alcoholic and acetal functional groups. The addition of an

¹ See Wesp and Brode, *J. Am. Chem. Soc.*, **56**, 1037 (1934).

² Davidson, *Ind. Eng. Chem., Anal. Ed.*, **12**, 40 (1940).

oxygen-containing compound causes the salt to distribute itself between the cellulose and the added compounds. Probably new complexes are formed by coordinate linkages of the mordant type. Since hydrocarbons and their halogen derivatives do not readily form complexes, they are not able to extract the red salt from the cellulose, and hence their solutions are not colored.

This test is especially valuable for subdividing the compounds in Class N₂. It distinguishes olefins and polyalkylbenzenes from the members of this solubility class which have an oxygen-containing functional group.

EXPERIMENT 12

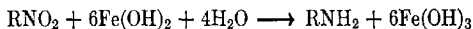
Ferrous Hydroxide

Add a small amount (about 10 mg.) of the compound to be tested to 1 ml. of the ferrous sulfate reagent (A) in a test tube, and then add 0.7 ml. of the alcoholic potassium hydroxide solution (B). Insert a glass tube so that it reaches the bottom of the test tube, and pass a stream of illuminating gas through the tube for about 30 seconds in order to remove air. Stopper the tube quickly, and shake. Note the color of the precipitate after 1 minute. Try the test on: (a) nitrobenzene; (b) *m*-nitroaniline; (c) ethyl alcohol; (d) isopropyl alcohol.

Reagents. (A) To 500 ml. of recently boiled, distilled water are added 25 g. of ferrous ammonium sulfate crystals and 2 ml. of concentrated sulfuric acid. An iron nail is introduced to retard oxidation by the air.

(B) Thirty grams of stick potassium hydroxide is dissolved in 30 ml. of distilled water, and this solution is added to 200 ml. of 95% ethanol.

Discussion. A positive test is indicated by the formation of a red-brown to brown precipitate. This is ferric hydroxide formed by oxidation of the ferrous hydroxide by the nitro compound, which in turn is reduced to the amine.



A negative test is indicated by a greenish precipitate. In some cases partial oxidation may cause a darkening of the ferrous hydroxide.

Practically all nitro compounds¹ give a positive test in about 30 seconds. The speed with which the nitro compound is reduced depends on its solubility. *p*-Nitrobenzoic acid, which is soluble in the alkaline reagent, gives a test almost immediately, whereas α -nitronaphthalene must be shaken about 30 seconds.

A positive test is also given by other compounds which oxidize ferrous hydroxide. Nitroso compounds, quinones, hydroxylamine, alkyl nitrates, and alkyl nitrites are in this group. Highly colored compounds cannot be tested.

EXPERIMENT 13

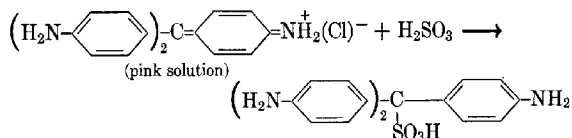
The Fuchsin-Aldehyde Reagent

Place 2 ml. of the fuchsin-aldehyde reagent in a test tube, and add 1 drop of butyraldehyde. Shake the tube gently, and observe the color developed in 3 to 4 minutes. Repeat the test with: (a) benzaldehyde; (b) formaldehyde solution; (c) acetophenone; (d) acetone.

In this test the reagent should not be heated, and the solution tested should not be alkaline. When the test is used on an unknown, a simultaneous test on a known aldehyde should be performed for comparison.

Reagent. Dissolve 0.5 g. of pure fuchsin (*p*-rosaniline hydrochloride) in 500 ml. of distilled water and filter the solution. Saturate 500 ml. of distilled water with sulfur dioxide, mix thoroughly with the filtered fuchsin solution, and allow to stand overnight. This produces a practically colorless and very sensitive reagent.

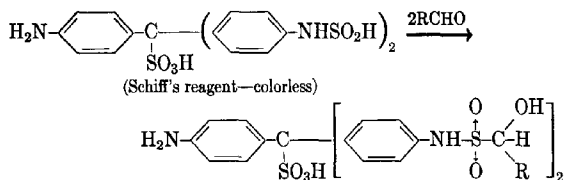
Discussion. Fuchsin is a pink triphenylmethane dye which is converted to the colorless leucosulfonic acid by sulfurous acid. Apparently the reaction involves 1,6-addition of sulfurous acid to the quinoid nucleus of the dye.²



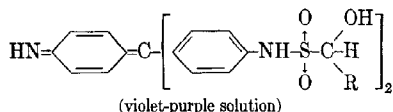
¹ Heaton and Gustavson, *Ind. Eng. Chem., Anal. Ed.*, **9**, 352 (1937).

² See Wieland and Scheuing, *Ber.*, **54**, 2527 (1921); Schlenk and Bergmann *Lehrbuch der organischen Chemie*, Vol. I, p. 262.

Sulfur dioxide reacts with this leucosulfonic acid to produce the *bis-N*-aminosulfonic acid which then combines with 2 moles of the aldehyde to produce the addition complex.



This leucosulfonic acid is unstable and loses sulfurous acid to produce a violet-purple quinoid dye.

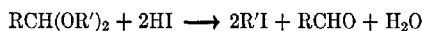
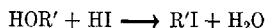
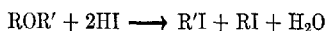


It is important to note that the color of this dye is different from that of the original fuchsin. The color is not a light pink but has a blue cast bordering on a violet or purple. Some ketones and unsaturated compounds react with sulfurous acid to regenerate the pink color of the fuchsin. The development of a light pink color in the reagent is, therefore, not a positive test for aldehydes.

The fact that certain compounds do cause the regeneration of the pink color of the original fuchsin has been made the basis of a test. It is reported that, when a specially prepared reagent¹ is used and the reaction time is 1 hour, aldoses produce a pink color whereas ketoses and disaccharides (except maltose) do not. This modification of the Schiff test must be employed with caution since many organic compounds produce a pink color with the reagent when shaken in the air; other compounds such as α,β -unsaturated ketones combine with sulfurous acid and thus reverse the first reaction given above.

¹ Tobie, *Ind. Eng. Chem., Anal. Ed.*, **14**, 405 (1942).

EXPERIMENT 14

Hydriodic Acid (Zeisel's Alkoxy Method)

Place about 0.1 g. (or 0.1 ml.) of the compound in a 16 by 150 mm. test tube. Carefully add, by means of a pipet, 1 ml. of glacial acetic acid and 1 ml. of 57% hydriodic acid (sp. gr. 1.7). Add a small piece of unglazed porcelain, and insert into the mouth of the test tube a gauze plug prepared as described below. The gauze plug is twisted so as to make a good fit and pushed down so that it is 4 cm. from the mouth of the test tube. A small piece of non-absorbent cotton is gently tamped on top of the plug by means of a glass rod so as to make a disc of cotton 2 to 3 mm. thick. A piece of filter paper about 2 by 10 cm. is folded longitudinally, moistened with a solution of mercuric nitrate, and placed on the cotton disc. The test tube is immersed to a depth of 4 to 5 cm. in an oil bath kept at 120° to 130°. It is convenient to use the melting-point apparatus shown in Fig. 1, page 19.

When the mixture boils, vapors rise through the tube and porous plug, which usually turns gray. The volatile alkyl iodide, rising through the plugs, reacts with the mercuric nitrate to produce a light orange or vermilion color due to the formation of mercuric iodide. A positive test consists in the formation of an orange or vermilion color on the test paper within a 10-minute heating period. A yellow color constitutes a negative or doubtful test.

Try this test on (1) anisole; (2) methyl benzoate; (3) α -methylglucoside.

Gauze Plugs. A solution of 1 g. of lead acetate in 10 ml. of water is added to 60 ml. of 1 *N* sodium hydroxide solution and stirred until the precipitate dissolves. To this sodium plumbite solution is added a solution of 5 g. of hydrated sodium thiosulfate in 10 ml. of water. About 1 ml. of glycerol is added, and the solution is diluted to 100 ml. About 5 ml. of this solution is pipetted

on strips of double cheesecloth 2 by 45 cm. The strips of cloth are dried and rolled to fit the test tube.

Mercuric Nitrate Solution. A saturated solution of mercuric nitrate is prepared in 49 ml. of distilled water to which has been added 1 ml. of concentrated nitric acid.

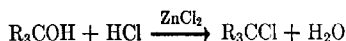
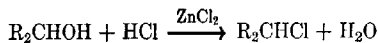
Discussion. This test¹ is based on the classic Zeisel method for estimating quantitatively the percentage of methoxyl or ethoxyl groups. Functional groups containing methyl, ethyl, *n*-propyl, or isopropyl radicals attached to oxygen are cleaved by the hydriodic acid with the formation of a volatile alkyl halide. Alkoxy derivatives in which the group is *n*-butyl or larger are difficult to cleave, and the iodide is too high-boiling to be volatilized. Some *n*-butoxy compounds give a positive test, but the procedure is not reliable (the boiling point of *n*-butyl iodide is 131°).

This class reaction is most useful for ethers, esters, and acetals in which the groups are methyl or ethyl. It is evident that methanol, ethanol, and the two propyl alcohols will also give a positive test. The test has been applied to numerous alkaloids and methylated sugars. The chief interference is caused by the presence of a sulfur-containing functional group which liberates hydrogen sulfide when heated with hydriodic acid.

Some ethers may require a more vigorous reagent² for cleavage. It is sometimes advantageous to use 2 ml. of the hydriodic acid, 0.1 g. of phenol, and 1 ml. of propionic anhydride for 0.1 g. of the sample.

EXPERIMENT 15

Hydrochloric Acid-Zinc Chloride. The Lucas Test



(a) To 1 ml. of the alcohol in a test tube add 10 ml. of the hydrochloric acid-zinc chloride reagent at 26–27°. Stopper the tube and shake the mixture; then allow the mixture to stand. Note the time required for the formation of the alkyl chloride, which appears as an insoluble layer or emulsion. Carry out the test on each of

¹ Tobie, *Ind. Eng. Chem., Anal. Ed.*, **15**, 433 (1943).

² Elek, *Ind. Eng. Chem., Anal. Ed.*, **11**, 174 (1939).

the following alcohols, and note by means of a watch the time required for the reaction to take place: (1) 1-butanol; (2) 2-pentanol; (3) 1-propanol; (4) *tert*-butyl alcohol; (5) isoamyl alcohol; (6) allyl alcohol; (7) benzyl alcohol.

Reagent. The hydrochloric acid-zinc chloride reagent is made by dissolving 136 g. (1 mole) of anhydrous zinc chloride in 105 g. (1 mole) of concentrated hydrochloric acid, with cooling.

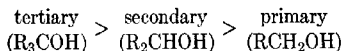
Discussion. The alcohols lower than hexyl are soluble in the reagent. Tertiary alcohols react at once to give two phases, the formation of which is indicated by the cloudy appearance of the mixture. Secondary alcohols react within 5 minutes to give a cloudy solution. In 10 minutes a distinct layer is usually observed. Saturated primary alcohols do not react at ordinary temperatures.

If there are impurities in the primary alcohols, some cloudiness may be observed. However, on standing, the second phase will not separate; for the secondary and tertiary alcohols the separation of the mixture into two layers after standing may serve as a check.

(b) To 1 ml. of the alcohol in a test tube add 6 ml. of concentrated hydrochloric acid. Shake the mixture, and allow to stand. Observe carefully during the first 2 minutes. Test the following alcohols, and record your results: (1) *n*-propyl alcohol; (2) 2-pentanol; (3) *tert*-butyl alcohol; (4) benzyl alcohol.

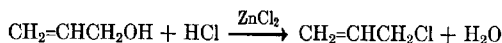
Discussion. The rate at which an alcohol is converted to an alkyl halide by the action of a halogen acid depends both on the nature of the acid and on the structure of the alcohol. For a given alcohol the order of reactivity of the halogen acids is the following: $\text{HCl} < \text{HBr} < \text{HI}$.

With a given hydrogen halide the alcohols react in the following order.



For example, tertiary alcohols react with concentrated hydrochloric acid so rapidly that the alkyl halide forms within a few minutes at room temperature. At first the mixture becomes milky; then the alkyl halide separates as an oily layer. Primary and secondary alcohols do not react appreciably under these conditions. However, if zinc chloride is present the secondary alcohol is converted to the corresponding chloride whereas the primary

alcohol remains unchanged. The latter must be heated for an extended period with the hydrochloric acid-zinc chloride mixture before it is changed to the chloride. Allyl alcohol is an exception; it reacts with the evolution of heat.



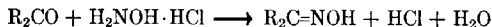
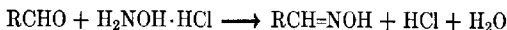
Allyl chloride may be caused to separate by diluting the mixture with ice water. The high reactivity of the hydroxyl group in allyl alcohol recalls that of the halogen atoms in allyl halides. In both instances the activation is to be traced to the ethylenic linkage.

For the behavior of hexyl alcohols and alcohols higher in the series, which are not soluble in water, and for further details of the method the student should consult the original literature.¹

Give the structural formulas and names of the isomeric five-carbon saturated alcohols which were not used in this experiment. How would they react with this reagent? How would you account for the difference in the behavior of allyl alcohol and *n*-propyl alcohol? Benzyl alcohol and *n*-amyl alcohol? What other methods can be used for classifying an unknown alcohol?

EXPERIMENT 16

Hydroxylamine Hydrochloride



(a) **For Neutral Compounds.** To 1 ml. of the reagent add a drop or a few crystals of the compound, and note the color change. If no pronounced change occurs at room temperature, heat the mixture to boiling. A change in color from orange to red constitutes a positive test. Try the test on: (1) *n*-butyraldehyde; (2) acetone; (3) benzophenone; (4) glucose.

(b) **For Acidic or Basic Compounds.** To 1 ml. of the indicator solution add about 0.2 g. of the compound, and adjust the color of the mixture so that it matches 1 ml. of the reagent in a separate test tube of the same size. This is done by adding a few drops of dilute (1%) sodium hydroxide or hydrochloric solution. Then add the resulting solution to 1 ml. of the reagent and note whether a red color is produced. Try this test on: (1) salicylaldehyde;

¹ See Lucas, *J. Am. Chem. Soc.*, **52**, 802 (1930).

(2) *p*-dimethylaminobenzaldehyde. Try the tests on tartaric acid by Procedures *a* and *b*.

Reagent. To a solution of 5 g. of hydroxylamine hydrochloride in 1 l. of 95% ethanol is added 3 ml. of Bogen or Grammercy Universal Indicator. The color of the solution is adjusted to a bright orange shade (pH 3.7 to 3.9) by adding dilute (5%) alcoholic sodium hydroxide solution dropwise. The reagent is stable for several months.

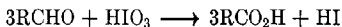
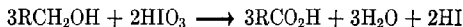
Indicator Solution. A solution of the indicator is made by adding 3 ml. of either of the above indicators to 1 l. of 95% ethanol.

Discussion.¹ The change in color of the indicator is due to the hydrochloric acid liberated in the reaction of the carbonyl compound with hydroxylamine hydrochloride, the oxime not being sufficiently basic to form a hydrochloride. All aldehydes and most ketones give an immediate change in color. Some higher-molecular-weight ketones such as benzophenone, benzil, benzoin, and camphor require heating. Sugars, quinones, and hindered ketones (such as *o*-benzoylbenzoic acid) fail to give a test.

Many aldehydes undergo autoxidation in the air and contain appreciable amounts of acids, hence the action of an aqueous solution or suspension on litmus must always be determined. If the solution is acidic, Procedure *b* must be used; this is also true of compounds whose solubility behavior places them in Class A₁, Class A₂, or Class B.

EXPERIMENT 17

Iodic Acid



This test is carried out by placing 20 ml. of the iodic acid reagent in a clean test tube and adding 1 drop or a small crystal of the compound to be tested. The tube is then kept in a beaker of boiling water for 1½ hours. At the end of this time the extent to which the compound has been oxidized is estimated by noting the amount of iodine that has been liberated. A deep brown solu-

¹ Duke, *Ind. Eng. Chem., Anal. Ed.*, **16**, 110 (1944).

tion constitutes a positive test, whereas a colorless or very light yellow solution indicates very little oxidation and hence a negative test.

Perform the test on the following compounds: methanol, ethanol, ethylene glycol, glucose, fructose. It is convenient to prepare the mixtures and heat them simultaneously. A control should be included for comparison.

Reagent. Twenty-three milliliters of concentrated sulfuric acid is added slowly, with stirring, to 78 ml. of distilled water. This solution is cooled to room temperature, and 1 g. of potassium iodate is added.

Discussion. Iodic acid exerts a selective oxidizing action on organic compounds. The following generalizations hold for the compounds with which the reagent has been used.¹

1. Simple aliphatic alcohols (up to octyl alcohol) are oxidized; methanol is an exception.

2. Polyhydric alcohols such as glycol, glycerol, erythritol, pentaerythritol, sorbitol, dulcitol, adonitol, mannitol, and inositol fail to be oxidized. Trimethylene glycol, pinacol, and propylene glycol are oxidized.

3. Aliphatic and aromatic aldehydes are oxidized.

4. Acetone, methyl ethyl ketone, and acetophenone are oxidized; benzophenone and benzil do not undergo oxidation.

5. Simple fatty and aromatic acids, including formic acid, give negative results. This is true also of glycolic, lactic, tartaric, citric, mucic, mandelic, and benzilic acids. α -Amino acids remain unoxidized except cystine, tyrosine, and tryptophane. Unsaturated acids, such as maleic and crotonic, also give negative results.

6. Glucose, mannose, galactose, and their derivatives as well as α -methylglucoside, pentaacetylglucose, glucosamine, maltose, and lactose fail to be oxidized appreciably.

7. Fructose and sorbose are oxidized; sucrose also undergoes oxidation (presumably because of fructose formation). Benzoin is unaffected.

8. The reagent oxidizes *d*-arabinose, *l*-xylose, and rhamnose (more slowly), presumably because of furfural formation.

9. Phenolic compounds as well as the phenyl ethers—anisole and phenetole—are oxidized.

10. All aniline derivatives are oxidized.

¹ Williams and Woods, *J. Am. Chem. Soc.*, **59**, 1408 (1937).

EXPERIMENT 18

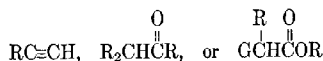
Mercuric Chloride-Sodium Ethoxide

To 1 ml. of the sodium ethoxide reagent (A) in a clean dry test tube add 2 drops of *n*-butyraldehyde. Mix the solutions and add 4 to 5 drops of mercuric chloride reagent (B). Shake vigorously and note the result. Try the test on: (a) acetone; (b) acetophenone; (c) ethyl acetoacetate; (d) anisole; (e) benzophenone. Carry out a control experiment in which no compound is added. Note the difference in the color of the precipitate.

Reagents. (A) The sodium ethoxide reagent is prepared by dissolving 1 g. of clean sodium in 100 ml. of absolute ethanol.

(B) The mercuric chloride reagent is prepared by dissolving 10 g. of mercuric chloride in 100 ml. of absolute ethanol. Both reagents are kept in bottles fitted with medicine droppers.

Discussion. This test is limited to neutral compounds in Classes S₁, S₂, N₁, and N₂ which contain only carbon, hydrogen, and oxygen. A positive test, which consists in the formation of a *white* (or occasionally light cream-colored) precipitate, is given by compounds which contain the structure



in which R may be hydrogen or an alkyl or aryl radical and G is an activating group such as the keto or ester grouping. Hence aldehydes or ketones which have at least one hydrogen atom on the α -carbon atom give a positive test. Esters such as ethyl malonate, ethyl acetoacetate, or their monoalkylated derivatives give a positive test. Acetylenic hydrocarbons with at least one hydrogen atom on a triply bound carbon atom give a positive test whereas all other hydrocarbons give a negative test. Ethers, alcohols, acetals, quinones, anhydrides, and simple esters give a negative test; this consists in the formation of a deep yellow precipitate similar to that formed when alcoholic solutions of mercuric chloride and sodium ethoxide are mixed.

Certain compounds such as anthrone, benzoin, furfuralacetophenone, mesityl oxide, and phenanthraquinone give such deep

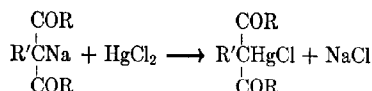
colors with sodium ethoxide solution alone that the color of the precipitate is obscured.

This test is especially valuable for distinguishing monoalkylated malonic or acetoacetic esters from the dialkyl derivatives. It is also useful in distinguishing aldehydes of the type RCH_2CHO or R_2CHCHO from those of the type R_3CCHO . Likewise, ketones of the type $R_3CC(=O)R_3$ and diaryl ketones give negative tests,

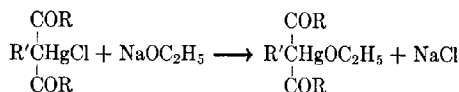


whereas ketones of the types RCH_2COR and R_2CHCOR give positive tests.

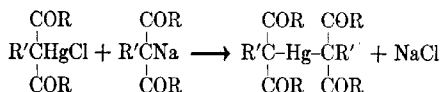
The exact structures of the products of this reaction have not been established. It seems possible that the sodium derivative of the compound reacts with the mercuric chloride to form the chloromercuri compound.



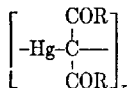
The latter may then react with a second mole of sodium ethoxide to give the ethoxymercuri derivative.



Or a second mole of the original sodium derivative may react forming a *bis*-mercuri compound.

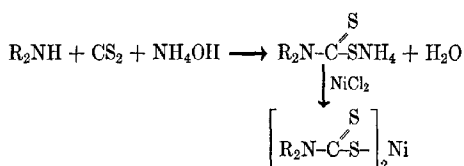


If in this *bis* compound R' is hydrogen a polymeric type of product may be formed.



Mercuric chloride also reacts with many other types of compounds. For a complete discussion of these reactions the student should consult the original literature.¹

EXPERIMENT 19

Nickel Chloride, Carbon Disulfide, and Ammonium Hydroxide²

Prepare an aqueous solution of the amine by adding 1 or 2 drops to 5 ml. of water. If necessary a drop or two of concentrated hydrochloric acid may be added to dissolve the amine. To 1 ml. of the reagent in a test tube, add 0.5 to 1 ml. of concentrated ammonium hydroxide, followed by 0.5 to 1 ml. of amine solution. A definite precipitate indicates a secondary amine. A slight turbidity is an indication of a trace of a secondary amine as an impurity. Try this test on: (1) aniline; (2) *N*-methylaniline; (3) triethylamine.

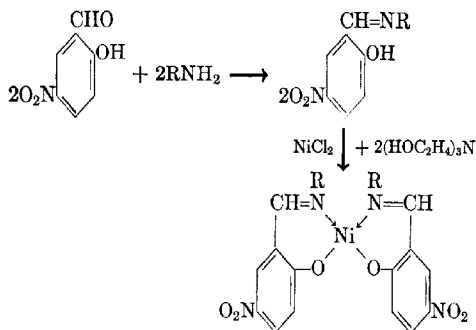
Reagent. To 0.5 g. of nickel chloride hexahydrate in 100 ml. of water is added an amount of carbon disulfide such that, after the mixture has been shaken, a globule of carbon disulfide is left on the bottom of the bottle. If stored in a tightly stoppered bottle, the reagent is stable for long periods of time. When the undissolved carbon disulfide evaporates, more must be added.

Discussion. This test is given by all secondary amines but not by primary amines. It is very sensitive, and certain commercial samples of tertiary amines produce turbidity due to the presence of small amounts of secondary amines. This is true of substituted pyridines, quinolines, and isoquinolines separated from coal-tar distillates.

¹ Connor and Van Campen, *J. Am. Chem. Soc.*, **58**, 1131 (1936).

² Duke, *Ind. Eng. Chem., Anal. Ed.*, **17**, 196 (1945).

EXPERIMENT 20

Nickel Chloride and 5-Nitrosalicylaldehyde ¹

To 5 ml. of water add 1 or 2 drops of the amine to be tested. If necessary a drop or two of concentrated hydrochloric acid may be added to dissolve the amine. Add 0.5 ml. of the resulting amine solution to 3 ml. of the reagent. An immediate copious precipitate is produced by a primary aliphatic amine, whereas primary aromatic amines usually require 2 to 3 minutes to give a definite precipitate. The appearance of a slight turbidity is not a positive test; it indicates that traces of primary amines may be present as impurities. Try the test on: (1) *n*-butylamine; (2) diethylamine; (3) aniline; (4) dimethylaniline.

Reagent. To 15 ml. of triethanolamine are added 0.5 g. of 5-nitrosalicylaldehyde (m.p. 124–125°) and about 25 ml. of water, and the aldehyde is brought into solution. Then 0.5 g. of nickel chloride hexahydrate dissolved in a few milliliters of water is added, and the total volume is brought to 100 ml. If the triethanolamine contains ethanolamine, it may be necessary to add another 0.5 g. of the aldehyde and remove the resulting precipitate by filtration.

Discussion. This test is so sensitive that care must be exercised in interpreting it. Only a definite precipitate produced in considerable quantity indicates a primary amine; a slight turbidity is merely indicative of impurities. Care must be taken to use the

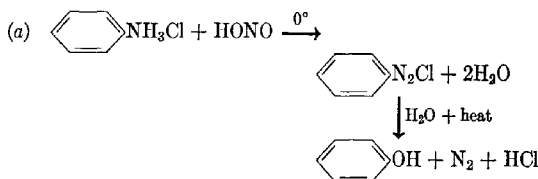
¹ Duke, *Ind. Eng. Chem., Anal. Ed.*, **17**, 196 (1945).

amounts specified above since the addition of large amounts of solutions of secondary amines will also give a precipitate. Many commercial samples of secondary and tertiary amines contain traces of primary amines and produce a turbidity.

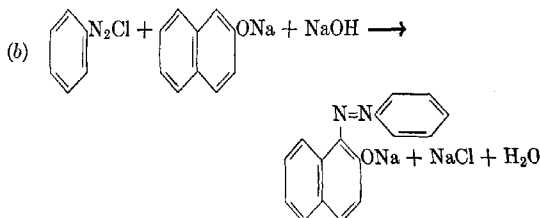
The test is given by all primary amines capable of forming the Schiff base with the 5-nitrosalicylaldehyde. Hydroxylamine and hydrazines substituted on only one nitrogen atom give positive tests. Amides do not give a precipitate. The test is not applicable to amino acids.

EXPERIMENT 21

Nitrous Acid



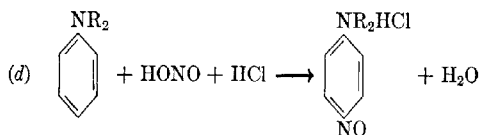
Diazotization. Dissolve 1 ml. of aniline in 3 ml. of concentrated hydrochloric acid diluted with 5 ml. of water, and cool the solution to 0° in a beaker containing cracked ice. Dissolve 1 g. of sodium nitrite in 5 ml. of water and add the solution slowly, with shaking, to the cold solution of aniline hydrochloride. Continue the addition until the mixture gives a positive test for nitrous acid. The test is carried out by placing a drop of the solution on starch-iodide paper; a blue color indicates the presence of nitrous acid. Remove 2 or 3 ml. of the solution to another test tube, warm gently, and observe the evolution of gas. What is formed? What is the term applied to the last reaction?



Coupling. Add a second portion of the cold diazonium solution—about 2 ml.—to a solution of 0.1 g. of β -naphthol in 2 ml. of 10% sodium hydroxide solution and 5 ml. of water. Note the formation of the orange-red dye.

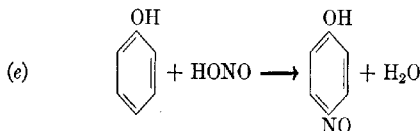


Dissolve 2 ml. of methylaniline in 5 ml. of concentrated hydrochloric acid, dilute with 5 ml. of water, and cool in an ice bath. Add slowly and with shaking 1.5 g. of sodium nitrite dissolved in 5 ml. of water, and note the result. What is the product? Is there any difference between aromatic and aliphatic secondary amines as far as this reaction is concerned?



Repeat test *c* using dimethylaniline. Note the color and character of the reaction product. Do tertiary aliphatic amines behave in the same manner?

Discussion. The action of nitrous acid on tertiary aromatic amines with substituents in the *para* position may cause nitration, demethylation, or cleavage and nitration.¹



Add a crystal of sodium nitrite to 2 ml. of concentrated sulfuric acid and shake until dissolved. Add 0.1 g. of phenol and note the changes in color. Pour the solution into 20 ml. of ice water and note the color. Add sodium hydroxide solution until the mixture is alkaline and again note the color.

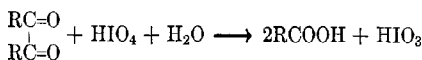
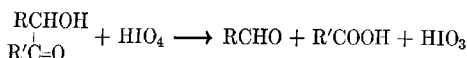
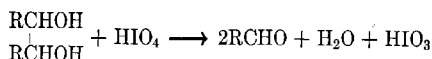
Discussion. This reaction, known as "Liebermann's nitroso" reaction, is characteristic of phenols in which an *ortho* or *para* position is unsubstituted. It may be used to test for the nitroso

¹ Pinnow, *Ber.*, **27**, 3161 (1894); Donald and Reade, *J. Chem. Soc.*, **1935**, 53. Crowley, Milton, Reade, and Todd, *J. Chem. Soc.*, **1940**, 1286.

grouping by mixing equal amounts of the nitroso compound and phenol, adding the mixture to sulfuric acid, and proceeding as in the above test.

EXPERIMENT 22

Periodic Acid



Place 2 ml. of the periodic acid reagent in a small test tube, add 1 drop (no more) of concentrated nitric acid, and shake thoroughly. Then add 1 drop or a small crystal of the compound to be tested. Shake the mixture for 10 to 15 seconds, and add 1 to 2 drops of aqueous silver nitrate solution (3%). The instantaneous formation of a *white* precipitate (silver iodate) indicates that the organic compound has been oxidized by the periodate which is thereby reduced to iodate. This constitutes a positive test. Failure to form a precipitate, or the appearance of a brown precipitate which redissolves on shaking, constitutes a negative test.

Apply the test to the following substances:¹ isopropyl alcohol, acetone, ethylene glycol, glycerol, glucose, formalin, tartaric acid, lactic acid.

Reagent. The periodic acid reagent is made by dissolving 0.5 g. of paraperiodic acid (H_5IO_6) in 100 ml. of distilled water.

Discussion. Periodic acid has a very selective oxidizing action² on 1,2-glycols, α -hydroxy aldehydes, α -hydroxy ketones, 1,2-diketones, and α -hydroxy acids. The rate of the reaction decreases in the order mentioned. Under the conditions specified above, α -hydroxy acids sometimes give a negative test.

It is important that the exact amounts of reagent and nitric acid be used. The test depends on the fact that silver iodate is

¹ For convenience these tests should be performed simultaneously.

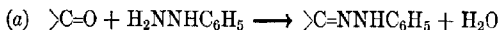
² Malaprade, *Compt. rend.*, **136**, 382 (1928); Fleury and Boisson, *ibid.*, **204**, 1264 (1937); Jackson and Hudson, *J. Am. Chem. Soc.*, **59**, 994 (1933).

only very slightly soluble in dilute nitric acid whereas silver periodate is very soluble. If too much nitric acid is present, however, the silver iodate will fail to precipitate.

Olefins, secondary alcohols, 1,3-glycols, ketones, and aldehydes are not affected by periodic acid under the above conditions. The periodic acid test is best suited for water-soluble compounds. For water-insoluble compounds dioxane solutions may be used.

EXPERIMENT 23

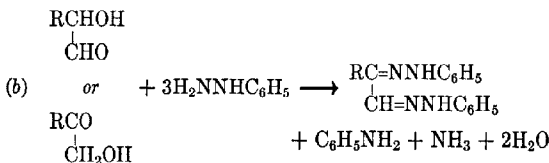
Phenylhydrazine ¹



To 5 ml. of water add 0.5 ml. of phenylhydrazine and then acetic acid drop by drop until the phenylhydrazine just dissolves. Then add 0.5 ml. of acetone and shake. If no precipitation occurs, warm gently for a minute in a low flame, add 2 ml. of water, and cool.

Dissolve 0.5 ml. of acetophenone in 2 ml. of ethanol, and add water dropwise until the cloudiness just disappears on shaking. If too much water is added, a little alcohol must be introduced to clarify the solution. To this clear solution add 0.2 ml. of pure phenylhydrazine. If the solution remains clear for several minutes, catalyze the reaction by the addition of a drop of acetic acid; warm gently for a few minutes and then cool. What advantage has this procedure over that given for acetone?

Osazones



Prepare 0.2-g. samples of glucose, maltose, sucrose, and galactose. Test the four sugars simultaneously in the following manner.

¹ This is the most useful reagent for aldehydes and ketones, and it is the first to be used on a neutral unknown. Phenylhydrazine decomposes when allowed to stand. If the acetic acid solution is not clear, it should be filtered. If the phenylhydrazine contains considerable tarry material, it should be redistilled before use.

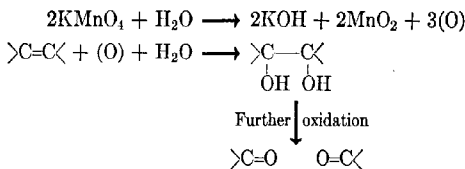
Place the samples in separate test tubes, and to each test tube add 0.4 g. of phenylhydrazine hydrochloride, 0.6 g. of crystalline sodium acetate, and 4 ml. of distilled water. Stopper the test tubes with one-holed corks, and place them together in a beaker of boiling water. Make a note of the time of immersion and of the time of precipitation of each osazone.¹ It is necessary to shake the tubes occasionally to avoid supersaturation.

After 20 minutes, remove the tubes from the hot water bath and set them aside to cool. After they are cool pour a small amount of the liquid and crystals on a watch glass. Tip the watch glass from side to side to spread out the crystals, and absorb some of the mother liquor with a piece of filter paper, taking care not to crush or break up the clumps of crystals. Examine the crystals under a low-power microscope (about 80–100 \times), and compare with photomicrographs.²

Discussion. The time required for the formation of the osazone is frequently a valuable aid in distinguishing between various sugars. Mulliken gives the following figures for the time required for the osazone to precipitate from the hot solution: fructose, 2 minutes; glucose, 4 to 5 minutes; xylose, 7 minutes; arabinose, 10 minutes; galactose, 15 to 19 minutes; raffinose, 60 minutes; lactose, osazone soluble in hot water; maltose, osazone soluble in hot water; mannose, $\frac{1}{2}$ minute (hydrazone); sucrose, 30 minutes, owing to hydrolysis and formation of glucosazone.

EXPERIMENT 24

Potassium Permanganate Solution

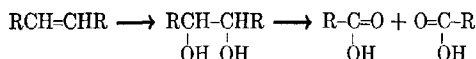


¹ The formation of tarry products due to oxidation of the phenylhydrazine may be prevented by the addition of 0.5 ml. of saturated sodium bisulfite solution. This should be done if it is desired to isolate the osazone and determine its melting point.

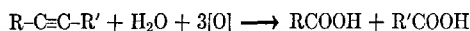
² Morrow and Sandstrom, *Biochemical Laboratory Methods*, 2nd ed., pp. 157–166, John Wiley & Sons, New York, 1935; Hassid and McCready, *Ind. Eng. Chem., Anal. Ed.*, **14**, 683 (1942).

To 2 ml. of water add 0.1 g. (or 0.2 ml.) of the compound to be examined. Then add a 2% potassium permanganate solution drop by drop with shaking until the purple color of the permanganate persists. Apply this test to: (a) 2-pentene; (b) toluene; (c) phenol; (d) benzaldehyde; (e) aniline; (f) formic acid; (g) cinnamic acid; (h) glucose. If the permanganate color is not changed in 0.5 to 1 minute, allow the tubes to stand for 5 minutes with occasional vigorous shaking. Do not be deceived by a slight reaction, for this may be due to the presence of impurities. In testing compounds insoluble in water it is usual to dissolve them in acetone free from methanol before trying the test. However, the test should always be tried on an aqueous suspension first.

Discussion. A solution of potassium permanganate is decolorized by compounds having ethylenic or acetylenic linkages. This is known as Baeyer's test for unsaturation. In cold dilute aqueous solutions the chief product of the action of potassium permanganate on an olefin is the glycol. If the reaction mixture is heated, further oxidation takes place, leading ultimately to cleavage of the carbon chain.



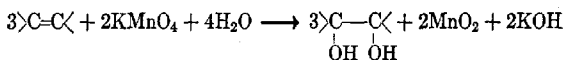
Acetylenic linkages are usually cleaved by oxidation and yield acids.



This test is general; in particular it is useful in connection with such compounds as tetraphenylethylene $(\text{C}_6\text{H}_5)_2\text{C}=\text{C}(\text{C}_6\text{H}_5)_2$ and tolane dibromide $(\text{C}_6\text{H}_5\text{CBr}=\text{CBrC}_6\text{H}_5)$, which do not decolorize a solution of bromine in carbon tetrachloride.

The speed with which unsaturated compounds decolorize permanganate depends on the solubility of the organic compound. If the compound is very insoluble it is necessary to powder the compound and shake the mixture vigorously for several minutes or to dissolve the substance in a solvent unaffected by permanganate.

Inspection of the following equation shows that, as the reaction proceeds, the solution becomes alkaline.



It is necessary, however, to avoid using a solution which is strongly alkaline, as this changes the nature of the test. In sodium carbonate solution, for example, even acetone gives a positive test. Frequently no actual precipitate of manganese dioxide is observed; the purple color gradually changes to a reddish brown.

However, the use of permanganate in neutral media is possible. Thus, if zinc permanganate is used, the zinc hydroxide produced is only slightly soluble and the solution remains practically neutral. Also, it is possible to use potassium permanganate in the presence of magnesium sulfate to accomplish this objective. In this case, the hydroxyl ion is precipitated in the form of insoluble magnesium hydroxide.

The Baeyer test, though superior to the bromine test for unsaturated compounds, offers in its turn certain complications. All easily oxidizable substances give this test. Carbonyl compounds which decolorize bromine solutions generally give a negative Baeyer test. Acetone is a good example of this; although it decolorizes bromine solutions rapidly, it can be used as a solvent in the Baeyer test. Aldehydes give a positive Baeyer test; however, many of them, such as benzaldehyde and formaldehyde, do not decolorize bromine solutions. Formic acid and its esters may be regarded as aldehydes for the purpose of this generalization since they also reduce permanganate.

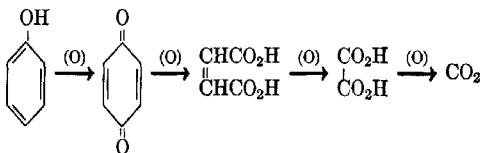
Alcohols form another important class of compounds which decolorize permanganate solutions but not bromine solutions. Secondary alcohols are more easily oxidized by neutral permanganate than primary alcohols. Practically all secondary alcohols decolorize the dilute potassium permanganate solution in 1 to 2 minutes. The soluble primary alcohols are oxidized more slowly but usually give a positive test within 3 minutes. Long-chain insoluble primary alcohols such as lauryl alcohol or cetyl alcohol do not reduce permanganate solution readily. Tertiary alcohols, provided that they are pure, do not reduce neutral permanganate immediately.

When acetone is used as a solvent in the Baeyer test it must be free from methyl alcohol and isopropyl alcohol. The solution must also be neutral.

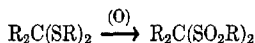
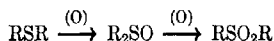
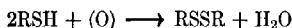
Compounds generally contain slight amounts of impurities which may decolorize permanganate solutions. For this reason,

the decolorization of only a drop or two of the permanganate solution cannot always be accepted as a positive test.

Phenols and arylamines also reduce permanganate solution and undergo oxidation to quinones; these may be further oxidized with an excess of the reagent to yield a series of oxidation products among which are maleic acid, oxalic acid, and carbon dioxide.



Organic sulfur compounds in which the sulfur is present in the reduced state also reduce permanganate and undergo oxidation. Mercaptans are oxidized to disulfides, and thio ethers and thio ketals to sulfoxes.

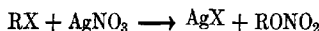


This oxidation of thio compounds takes place more readily in an acid medium. Hence, if the elementary analysis shows the presence of sulfur, it is desirable to dissolve 0.1 g. of the compound in 2 ml. of glacial acetic acid and add the dilute potassium permanganate solution drop by drop. If the purple color is discharged, the presence of an oxidizable sulfur-containing functional group is a possibility. When the sulfur is present in the form of sulfoxes, alkyl sulfates, or unsubstituted sulfonic acids, the permanganate solution is not reduced. However, certain substituted sulfonates, such as aldehyde and ketone bisulfite compounds, and phenolic sulfonic acids do reduce permanganate.

What functional groups respond to both the bromine and the permanganate tests? Which of these tests is better for detecting the presence of multiple bonds? In what instances is it helpful to use both reagents? Why is acetone a satisfactory solvent for the permanganate test?

EXPERIMENT 25

Silver Nitrate Solution (Alcoholic)

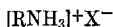


This reagent is useful for classifying compounds known to contain halogen. Add 1 drop of the halogen compound to 2 ml. of a 2% ethanolic silver nitrate solution. If no reaction is observed after 5 minutes' standing at room temperature, heat the solution to boiling and note whether a precipitate is formed. If there is a precipitate, note its color. Add 2 drops of dilute (5%) nitric acid, and note whether the precipitate dissolves. Silver halides are insoluble in dilute nitric acid, whereas silver salts of organic acids are soluble.

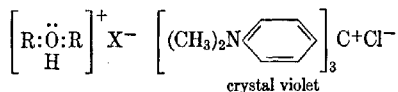
Apply the test to: (1) benzoyl chloride; (2) benzyl chloride; (3) ethyl bromide; (4) bromobenzene; (5) chloroform; (6) chloroacetic acid. In carrying out this test, care must be taken to distinguish between a slight cloudiness in the reaction mixture (due to traces of halogen) and a definite precipitate of silver halide.

Discussion. Many halogen-containing substances react with silver nitrate to give an insoluble silver halide, and the rate of this reaction is an index of the degree of reactivity of the halogen atom in question. This information is valuable since it permits certain deductions to be drawn concerning the structure of the molecule.

The degree of activity of the halogen atom depends to a very large extent on the type of radical to which it is attached. The following generalizations are useful. The most reactive halogens are those which are ionic. Among organic compounds the amine salts of the halogen acids constitute the most common examples.



Less frequently encountered are oxonium salts and carbonium salts which contain ionic halogen.



Aqueous solutions of these salts give an immediate precipitate of the silver halide with aqueous silver nitrate solution.

The reactivity of covalently bound halogen depends on (1) the nature of the halogen, (2) the carbon skeleton to which it is attached, and (3) the nature and proximity of other functional groups. In regard to the first of these factors, numerous studies have shown that the general order of reactivities of halides is $I > Br > Cl$. However, there is usually observed a larger difference between chlorides and bromides than between bromides and iodides. In fact, toward not a few common reagents many chloro compounds exhibit a low order of reactivity.

No direct comparisons (using the same reagent, solvent, and temperature) have been made relating the reactivity of alkyl

TABLE XV

Bond	Bond Energy * kcal./mole	Bond Distance * Å	Bond Refrac- tivities † P_E	Electro- negativity Differences * $X_A - X_B$
C-F	107.0	1.41	1.60	1.5
C-Cl	66.5	1.76	6.57	0.5
C-Br	54.0	1.91	9.47	0.3
C-I	45.5	2.10	14.57	0.0

* From Pauling, *The Nature of the Chemical Bond*, Cornell Univ. Press, Ithaca, N. Y., 1945.

† From Smyth, *Dielectric Constant and Molecular Structure*, Chemical Catalog Co., New York, 1931.

fluorides with the other alkyl halides. However, the fluorides generally are less reactive than the corresponding chlorides. Table XV contains some data on the physical properties of the various carbon-halogen linkages. These data show that the carbon-fluorine linkage, for example, is more stable than the carbon-chlorine linkage. From these data it follows that the relative reactivities of the halides toward reagents tending to remove the halogen would be in the order $RI > RBr > RCl > RF$.

The reactivity of an *alkyl halide* depends on whether it is primary, secondary, or tertiary; the order is tertiary > secondary > primary. The following butyl bromides illustrate this point; they are arranged in decreasing order of reactivity.



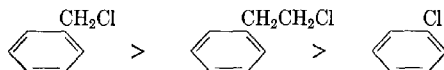
Alicyclic halides exhibit a decreased reactivity when compared with the corresponding open-chain secondary halides. Cyclo-

hexyl chloride is inactive, and cyclohexyl bromide is less reactive than 2-bromohexane, although it will give a precipitate with alcoholic silver nitrate.

The position of a double bond relative to the halogen atom is of paramount importance. Vinyl halides are generally inert; allyl halides are very reactive; and other types of halogenated olefins usually fall between these two extreme types. Thus, allyl chloride is more reactive than 4-chloro-1-butene, which in turn is more reactive than 1-chloro-1-propene.

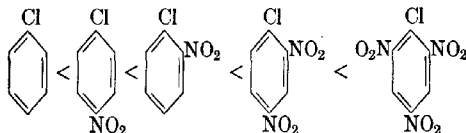


It is interesting to note that this generalization holds also for the influence of a double bond which is a part of a benzenoid ring. Chlorobenzene, like vinyl chloride, is unreactive, whereas benzy. chloride resembles allyl chloride and shows a high degree of reactivity. β -Phenylethyl chloride is intermediate in reactivity.



Although aryl halides generally do not react with alcoholic silver nitrate, the introduction of substituents may induce reactivity. The halogen atom is reactive when situated in the *ortho* or *para* positions with respect to certain groups which are *meta*-directing in their orienting influence. However, not all *meta*-directing groups exert this activating influence.¹

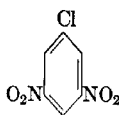
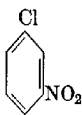
The most pronounced effect is observed in the nitro-substituted aryl halides. An increase in the number of nitro groups *ortho* and *para* to the halogen increases the ease with which the halogen atom is removed. The following compounds, illustrating this effect, are arranged in the order of increasing reactivity.



Introduction of nitro groups in the *meta* position causes very little change in reactivity of the halogen. Thus, the reactivity of

¹ Todd and Shriner, *J. Am. Chem. Soc.*, **56**, 1382 (1934).

m-nitrochlorobenzene and 3,5-dinitrochlorobenzene is of the same order as that of chlorobenzene.



This difference in the effect of groups in the *ortho* and *para* positions as compared with the same group in the *meta* position follows from the principle of vinylogy.¹ *o*-Nitrochlorobenzene and *p*-nitrochlorobenzene are vinylogs of ClNO_2 which has a very reactive halogen, whereas *m*-nitrochlorobenzene is not a vinylog of this parent compound.

Usually, when the halogen atom is held by a carbon atom joined to an oxygen atom, the reactivity will be great. Acid chlorides and α -halogen ethers are examples of compounds that give an immediate precipitate with alcoholic silver nitrate.

The reactivity of halogen atoms which are *alpha* to a carbonyl group depends on the halogen. α -Chloro ketones, acids, esters, and nitriles do not react at room temperature, whereas the corresponding α -bromo and α -iodo derivatives react immediately. β -Chloro- and β -bromoethers have anomalous reactivities² and do not give a precipitate with ethanolic silver nitrate. The halogen in α -halogen ketones is removed readily by alkaline reagents such as alcoholic potassium hydroxide or aqueous sodium acetate. If the elementary analysis for halogen is positive but the alcoholic silver nitrate test is negative it is advisable to boil a small amount of the compound with alcoholic sodium ethoxide or alcoholic sodium acetate for 10 minutes. The mixture is diluted with twice its volume of distilled water, cooled, acidified with dilute nitric acid, and filtered. If the filtrate is cloudy, it is clarified with a drop or two of ethanol, and silver nitrate solution is added. This modified procedure will give a positive test for compounds such as ω -chloroacetophenone which do not give a precipitate with alcoholic silver nitrate directly.

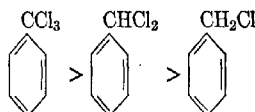
The accumulation of chlorine atoms on the same carbon atom in simple aliphatic compounds brings about a remarkable degree

¹ Fuson, *Chem. Revs.*, **15**, 1 (1935).

² Kirner, *J. Am. Chem. Soc.*, **48**, 2745 (1926); Fuson, Little, and Miller *ibid.*, **60**, 2404 (1938).

of inertness to silver nitrate such as is seen in chloroform, carbon tetrachloride, *s*-tetrachloroethane, and trichloroacetic acid. This is not true of bromo compounds; carbon tetrabromide reacts with silver nitrate at 25°, and bromoform and *s*-tetrabromoethane give a precipitate with boiling alcoholic silver nitrate.

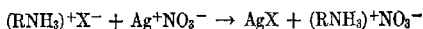
In compounds of the allyl chloride type accumulation of chlorine atoms on a single carbon atom does not decrease their reactivity but actually seems to increase it. Benzotrichloride is more easily hydrolyzed than benzal chloride, which in turn is more reactive than benzyl chloride.



It is convenient to utilize both aqueous and alcoholic silver nitrate solutions in classifying halogen compounds according to the reactivity of the halogen atoms.

I. Water-soluble compounds giving an immediate precipitate with aqueous silver nitrate.

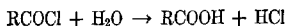
1. Amine salts of halogen acids.



2. Oxonium salts.

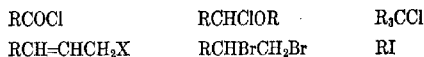
3. Carbonium halides.

4. Low-molecular-weight acid chlorides. Many of these are hydrolyzed by water and so furnish the halide ion.

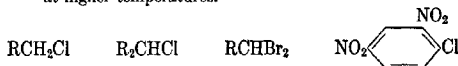


II. Water-insoluble compounds fall roughly into three groups with respect to their behavior toward alcoholic silver nitrate solutions.

1. Compounds in this group give an immediate precipitate at room temperature



2. The second group includes compounds which react slowly or not at all at room temperature but give a precipitate readily at higher temperatures.



3. A final group is made up of compounds which are inert toward hot alcoholic silver nitrate solutions.



The reactivity of a halogen atom in an organic compound depends on the reagent which is employed. For example, the use of sodium iodide in acetone will give an order of reactivity different from that noted for silver nitrate solutions (see Experiment 30, p. 140).

EXPERIMENT 26

Sodium



To 1 ml. of *n*-butyl alcohol add thin slices of metallic sodium until no more will dissolve. Cool the solution and observe. Add an equal volume of ether. What is the precipitate? Apply the test to acetone, *n*-butyl ether, and toluene.¹

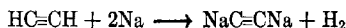
Discussion. This reagent is of most value in testing *neutral* compounds for the presence of groups which contain easily replaceable hydrogen atoms. Functional groups containing a hydrogen atom attached to oxygen, nitrogen, or sulfur react with sodium to liberate hydrogen.



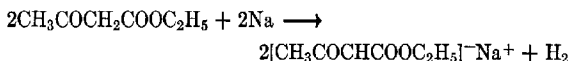
This test is most useful in connection with the alcohols of intermediate molecular weight, i.e., those containing from three to about eight carbon atoms. Lower alcohols are difficult to obtain in anhydrous condition. The presence of traces of moisture causes the test to be positive. Alcohols of high molecular weight react slowly with sodium, and the evolution of gas is often so slow as to make the test of little value. Metallic sodium when cut in moist air adsorbs water on its surface so that, when placed in a perfectly dry solvent such as benzene, it gives off hydrogen produced by the interaction of the metal with the adsorbed moisture.

¹ This test may be applied to solid compounds or very viscous liquids by dissolving them in an inert solvent such as anhydrous ligroin or benzene.

Hydrogen atoms attached to carbon are not displaced by metals unless there are adjacent functional groups which activate the hydrogen atoms. Compounds with active methine groups, such as acetylene or monosubstituted acetylenes, react with sodium.



A methylene group adjacent to an activating group and especially between two such groups possesses hydrogen atoms which may be displaced by sodium.



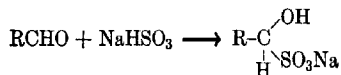
Reactive methyl groups are present in certain compounds, especially methyl ketones such as acetone and acetophenone. These react with sodium to give the sodium derivative of the ketone and a mixture of products formed by reduction and condensation. For example, acetone yields sodium acetone, sodium isopropoxide, sodium pinacolate, mesityl oxide, and phorone.

Metallic sodium is thus a useful reagent for detecting those types of reactive hydrogen compounds which are not sufficiently active to produce hydrogen ions in an ionizing solvent. It is obviously unnecessary to try the action of sodium on compounds in Class A₁ or A₂ or on compounds in Class S₁ or S₂ which give aqueous solutions acid to litmus.

Predict the action of sodium on phenol, benzoic acid, oximes, nitromethane, and benzenesulfonamide. Why is this test never used with these compounds? What effect would the presence of moisture have on this test? What is the principal defect of metallic sodium as a classification reagent?

EXPERIMENT 27

Sodium Bisulfite Solution



Prepare an alcoholic solution of sodium bisulfite by adding 3 ml. of ethanol to 12 ml. of a 40% aqueous solution of the salt. A small amount of salt will be precipitated by the alcohol and

must be separated by decantation or filtration before the reagent is ready for use.

Place 1 ml. of the reagent in a test tube and add 0.3 ml. of benzaldehyde. Stopper the test tube and shake vigorously. Repeat the test with: (a) heptaldehyde; (b) acetophenone.

Discussion. The formation of bisulfite addition compounds is a general reaction of aldehydes. Most methyl ketones, low-molecular-weight cyclic ketones (up to cyclooctanone), and certain other compounds having very reactive carbonyl groups behave similarly. Some methyl ketones, however, form the addition compounds only slowly or not at all. Examples are aryl methyl ketones, pinacolone, and mesityl oxide. On the other hand, cinnamaldehyde forms an addition compound containing two molecules of bisulfite.

The bisulfite addition compounds are believed to be hydroxy-sulfonates;¹ this type of structure has been proved to be correct for the derivatives of formaldehyde² and acetaldehyde.³

The bisulfite is in equilibrium with the carbonyl compound, and, since sodium bisulfite is decomposed by either acids or alkalies, the addition compounds are stable only in neutral solutions. Those compounds derived from low-molecular-weight carbonyl compounds are soluble in water. They are useful because they are solids—easily purified, and because they are readily decomposed by acids and by alkalies to regenerate the original compounds.

Suggest an explanation of the fact that cyclohexanone reacts with sodium bisulfite readily whereas diethyl ketone does not. What is the explanation of the failure of pinacolone to react? Compare this case with that of acetophenone. Explain the behavior of cinnamaldehyde. Why is an alcoholic solution of sodium bisulfite used? Try the test on acetone, using an aqueous solution.

EXPERIMENT 28

Sodium Hydroxide Solution

Acids

Neutralization Equivalent



¹ See Raschig and Prah, *Ber.*, **61**, 179 (1928).

² Lauer and Langkammerer, *J. Am. Chem. Soc.*, **57**, 2360 (1935).

³ Shriner and Land, *J. Org. Chem.*, **6**, 888 (1941).

Procedure. A sample of the acid (about 0.2 g.) is weighed accurately and dissolved in 50 to 100 ml. of water or ethanol. The mixture may be heated if necessary to dissolve all the compound. This solution is titrated with a previously standardized sodium hydroxide solution having a normality factor (N.F.) of about 0.1, phenolphthalein being used as the indicator. The neutralization equivalent of the acid is calculated according to the formula

$$\text{Neutralization equivalent} = \frac{\text{Weight of sample} \times 1000}{\text{Volume of alkali (ml.)} \times \text{N.F.}}$$

Discussion. The molecular weight of an acid may be determined from the neutralization equivalent by multiplying that value by the number of acidic groups in the molecule. Acids may also be titrated in a solvent composed of ethanol and benzene or toluene.

A blank must always be run on the solvent; the same amount of phenolphthalein which was used in the titration must be employed in the blank. In ordinary work the neutralization equivalents should check the calculated values within $\pm 1\%$. By use of carefully purified and dried samples and good technic the error may be reduced to $\pm 0.3\%$.

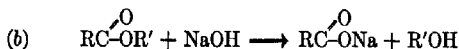
In order to give an accurate neutralization equivalent the substance titrated must be pure and anhydrous. If the value obtained for the neutralization equivalent does not check the theoretical value, the compound should be recrystallized from a suitable solvent and carefully dried.

Amine salts of strong acids may be titrated by the same procedure.

Questions

1. If an acid is imperfectly dried, will the neutralization equivalent be high or low?
2. Would the presence of an aromatic amino group interfere in the determination of the neutralization equivalent? What would be the effect of an aliphatic amino group?
3. What types of phenols may be titrated quantitatively?
4. From a theoretical point of view, what should the ionization constant of an acid be in order that the acid may be titrated with phenolphthalein?

Esters



Method A. In a round-bottomed flask fitted with an efficient reflux condenser place 40 ml. of a 25% sodium hydroxide solution. Add 5 ml. of ethyl benzoate and heat to boiling. A piece of porous plate or a boiling tube should be placed in the flask to prevent bumping. Continue the boiling until the ester layer or the characteristic odor disappears (about half an hour). Reverse the condenser, distil about 5 ml., and saturate the distillate with potassium carbonate. Note the formation of two layers. Explain. The amount of sample required will obviously depend on the molecular weight of the alcohol to be isolated as well as upon the molecular weight of the original ester.

Cool the residue in the flask, and acidify with dilute phosphoric acid. What is the solid which separates? How can you be sure that it is not sodium phosphate? If the acid were a volatile liquid it could be separated by distillation.¹

Discussion. Esters vary considerably in the ease with which they may be saponified. Most simple esters boiling below 110° will be saponified completely by refluxing with 25% sodium hydroxide solution for $\frac{1}{2}$ hour as described in Method A above. Esters boiling between 110 and 200° require a longer time (1 to 2 hours) for complete saponification.

The hydrolysis of water-insoluble esters may be markedly accelerated by the addition of 0.1 g. of sodium lauryl sulfate (Gardinol) to the alkali and the ester. The mixture is shaken vigorously to emulsify the ester and is then heated to refluxing. A large flask must be used since the emulsifying agent causes considerable foaming.

Very high-boiling esters (above 200°) which are insoluble in water hydrolyze slowly, and prolonged refluxing may result in loss of a volatile alcohol. The following procedure² utilizes a solution of potassium hydroxide in diethylene glycol (b.p. 244°). Diethylene glycol is not only an excellent solvent for esters but also permits the use of a higher reaction temperature, and all but high-boiling alcohols can be distilled from the reaction mixture in a pure state.

Method B. In a 10- or 25-ml. distilling flask place 3 ml. of diethylene glycol, 0.5 g. of potassium hydroxide pellets, and 0.5 ml. of water. Heat the mixture over a low flame until the

¹ See the method of determining Duclaux numbers described on page 146.

² Redemann and Lucas, *Ind. Eng. Chem., Anal. Ed.*, 9, 521 (1937).

alkali has dissolved, and cool; add 1 to 2 g. of the ester, and mix thoroughly. Attach a thermometer by means of a cork, and arrange a test tube cooled by a beaker of ice as a receiver. The flask is heated over a small flame at first, and the contents are mixed by shaking. When only one liquid phase or one liquid and one solid phase are present the mixture is heated more strongly so that the alcohol distils. The distillate is used for the preparation of a solid derivative such as the 3,5-dinitrobenzoate.

The residue in the flask is either a solution or suspension of the potassium salt of the acid derived from the ester. Add 10 ml. of water and 10 ml. of ethanol to the residue, and shake thoroughly. Add dilute sulfuric acid (6 *N*) until the solution is slightly acid to phenolphthalein. Allow the mixture to stand about 5 minutes and then filter. The filtrate is used directly for the preparation of a derivative. It may be treated with *p*-nitrobenzyl bromide or *p*-phenylphenacyl bromide in order to obtain the corresponding solid ester. If the original ester was so high boiling that a good boiling point could not be obtained, it may be desirable to divide the filtrate in half and make two derivatives.

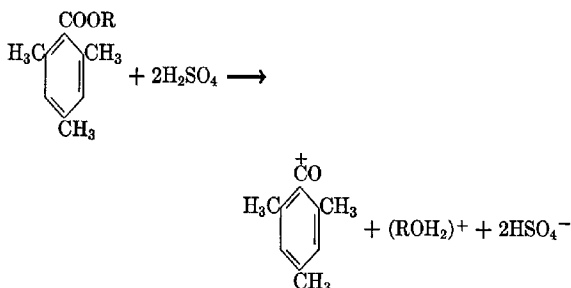
Discussion. Saponification represents the most useful procedure for characterizing esters. However, it must be remembered that hot concentrated alkali also affects other functional groups. Aldehydes which have α -hydrogen atoms undergo the aldol condensation and resinification. Aldehydes which have no α -hydrogen atoms undergo Cannizzaro's reaction and form an alcohol and the sodium salt of an acid.



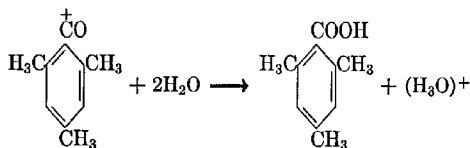
Polyfunctional compounds such as β -diketones and β -keto esters undergo cleavage under the influence of hot alkalies. The possibility of such interfering reactions is detected by means of the other classification reagents mentioned in this chapter and emphasizes the fact that *a single classification reagent cannot be taken as proof of the presence of a certain functional group*. It is important to correlate all the tests in attempting to draw conclusions concerning the structure of an unknown compound.

Mention should be made of the fact that esters of sterically hindered acids, such as alkyl 2,4,6-trialkylbenzoates, are very difficult to hydrolyze with alkali. However, these esters may be hydrolyzed rapidly by dissolving them in 100% sulfuric acid and

diluting the solution with ice water.¹ This result is due to the fact that esters of sterically hindered acids undergo the following reaction when dissolved in 100% sulfuric acid.²



When water is added, the carbonium ion forms the acid.



Conversely, the sterically hindered acid may be converted readily to an ester by dissolving it in 100% sulfuric acid and treating the solution with the alcohol.

Unhindered esters do not undergo these reactions. They dissolve in 100% sulfuric acid and are recovered unchanged when the solution is poured into ice water.

Esters of sterically hindered acids and alcohols such as *tert*-butyl 2,4,6-trimethylbenzoate, though extremely resistant to hydrolysis by alkalies, may be hydrolyzed readily by boiling for 1 hour with 18% hydrochloric acid.³

Show by equations the products formed by the alkaline hydrolysis of: (a) *p*-phenylphenacyl acetate; (b) ethylene glycol dibenzoate; (c) *n*-butyl oxalate; (d) the polyester of glycerol and phthalic acid. Devise suitable procedures for detecting the products formed in these reactions.

¹ Newman, *J. Am. Chem. Soc.*, **63**, 2431 (1941).

² Hammett, *Physical Organic Chemistry*, pp. 45-49, 278-281, McGraw-Hill Book Co., New York, 1940.

³ Cohen and Schneider, *J. Am. Chem. Soc.*, **63**, 3382 (1941).

Saponification Equivalents of Esters

Diethylene Glycol Method. *The Preparation of a Solution of Potassium Hydroxide in Diethylene Glycol.* The reagent is made by dissolving 3 g. of C.P. potassium hydroxide pellets in 15 ml. of diethylene glycol. It is necessary to warm the mixture gently to effect solution. A thermometer should be used for stirring, and the mixture should not be heated above 130°; higher temperatures may cause the reagent to be colored. After all the solid has dissolved the warm solution is poured into 35 ml. of diethylene glycol contained in a glass-stoppered bottle. The solution is mixed thoroughly and allowed to cool. It is approximately 1.0 *N* and is standardized by pipetting 10 ml. into a flask, adding 10 ml. of water, and titrating with a previously standardized 0.25 *N* hydrochloric acid solution.

The Saponification of the Ester. Exactly 10 ml. of the reagent is pipetted into a small glass-stoppered Erlenmeyer flask. The ester is placed in a small weighing bottle fitted with a small pipet. The weight of the bottle, ester, and pipet is determined, and a sample of 0.4 to 0.6 g. of the ester is transferred to the reagent in the Erlenmeyer flask by means of the pipet, which is then returned to the weighing bottle. The loss in weight of the bottle represents the weight of the sample.

The ester is mixed with the reagent by a rotary motion of the flask. The stopper is held firmly in place and the mixture heated in an oil bath so that a temperature of 70–80° is reached in 2 to 3 minutes. The liquid is agitated by a whirling motion during heating. At this point the flask is removed from the heating bath and shaken vigorously. The liquid is allowed to drain and the stopper is carefully loosened to allow air to escape (caution!). The stopper is replaced, and the temperature is raised to 120–130°. With very high-boiling esters the stopper may be removed and a thermometer inserted.

After 3 minutes at this temperature the flask and its contents are cooled to 80–90° and the stopper is removed and washed with distilled water so that the rinsings drain into the flask. About 15 ml. of distilled water is added; the contents are mixed and then titrated with 0.25 *N* hydrochloric acid using phenolphthalein as

the indicator. The saponification equivalent is calculated according to the following equation.

Saponification equivalent =

$$\frac{\text{Weight of sample} \times 1000}{(\text{Volume of alkali [ml.]} \times \text{N.F.}) - (\text{Volume of acid [ml.]} \times \text{N.F.})}$$

Discussion. The above procedures give complete saponification of esters which are insoluble in water. Esters such as benzyl acetate, butyl phthalate, ethyl sebacate, butyl oleate, and glycol and glycerol esters are completely saponified.¹

Alcoholic Sodium Hydroxide Method. *The Preparation of an Alcoholic Sodium Hydroxide Solution.* Eight grams of sodium is dissolved in 250 ml. of absolute ethanol, and, after solution is complete, 25 ml. of water is added. This solution is standardized by titration with a previously standardized 0.25 *N* hydrochloric acid solution or by direct titration against a weighed sample of pure potassium acid phthalate.

The Saponification of the Ester. The ester is placed in a weighing bottle containing a small pipet. The weight of the bottle and pipet is determined, and a sample of 0.2 to 0.4 g. of the ester is transferred to a 150-ml. Erlenmeyer flask by means of the pipet, which is then returned to the weighing bottle and the two again weighed. The loss in weight is the weight of the sample. Fifteen milliliters of the above alcoholic sodium hydroxide solution, measured from a buret, is then added to the flask containing the ester. The flask is attached to an efficient reflux condenser by means of a carefully cleaned rubber stopper, and the mixture is refluxed gently for 1¼ to 1½ hours. At the end of this time the mixture is allowed to cool slightly. The flask is loosened from the condenser, and the rubber stopper and condenser tube are washed with a stream of water from a wash bottle, the washings being allowed to run into the saponification mixture. Two drops of phenolphthalein solution is added, and the excess alkali is titrated by means of 0.25 *N* hydrochloric acid. The end point should be a faint pink. It is best to titrate the solution until the phenolphthalein is colorless and then back-titrate with the original alkali.

¹ Redemann and Lucas, *Ind. Eng. Chem., Anal. Ed.*, **9**, 521 (1937).

Discussion. The ester must be pure and anhydrous in order to give an accurate saponification equivalent. The following precautions must be observed in order to obtain accurate results.

1. The alcoholic sodium hydroxide solution should be standardized immediately before use and its normality factor (N.F.) recorded.

2. The standard solutions should be measured accurately from a buret, since a slight error in the amount of alkali will cause a large error in the saponification equivalent. This is especially noticeable with high-molecular-weight esters.

3. Refluxing for $1\frac{1}{2}$ hours will saponify most esters. For some, a longer time (2 to 24 hours) may be necessary.

4. Corks must not be used to attach the flask to the condenser since the alcohol vapors extract substances which lower the strength of the alkali. Rubber stoppers, cleaned by warming with dilute alkali and then thorough washing with distilled water, should be used.

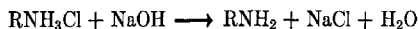
5. The end point should be a faint pink. This is the color assumed by phenolphthalein at pH 9.0, which represents the hydrogen-ion concentration of solutions of the sodium salts of most organic acids.

6. The molecular weight of the ester is equal to N times the saponification equivalent, where N is the number of ester groups in the molecule.

Questions

1. What saponification value would be obtained for ethyl acetoacetate? *n*-butyl β -bromopropionate? ethyl hydrogen phthalate? ethyl cyanoacetate?
2. What would happen if the above procedure was applied to benzaldehyde?
3. If an ester had already partially hydrolyzed, what effect would this have on the saponification equivalent?

Ammonium Salts and Amine Salts

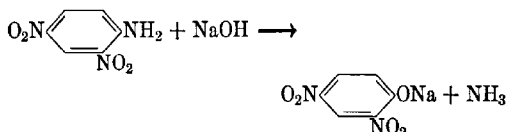
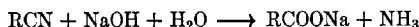
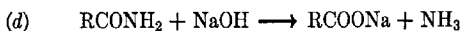


Place 5 ml. of 10% sodium hydroxide solution in a test tube, add 0.2 g. of ammonium benzoate, and shake the mixture vigorously. Note the odor of ammonia.

To 0.4 g. of aniline hydrochloride in a test tube add 5 ml. of 10% sodium hydroxide solution. Shake the mixture and allow

it to stand a few minutes. Note the separation of the oily layer of the amine.

Amides, Substituted Amides, and Nitriles



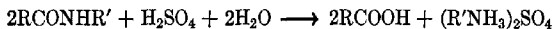
Treat 5 ml. of 10% sodium hydroxide solution in a test tube with 0.2 g. of urea. Shake the mixture, and note whether ammonia is evolved. Repeat the test with: (a) benzamide; (b) acetanilide; (c) benzonitrile; (d) 2,4-dinitroaniline. Then heat each of the mixtures to boiling and note the odor. Test the action of the vapors on moist pink litmus paper.

Cool the above solutions, and acidify each with hydrochloric acid. Note the result. What determines whether a precipitate forms?

Discussion. The ammonia or amine which is the product of this alkaline hydrolysis may be characterized by the Hinsberg test or by use of reagents in Experiments 19 and 20. For this purpose it is best to use a larger sample (1 g.) and distil the ammonia or volatile amine from the alkaline solution into a receiver containing dilute hydrochloric acid. This solution may then be neutralized and tested as directed in Experiment 4.

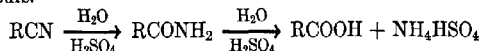
A water-insoluble amine may be removed by extraction with ether. The ether can then be distilled and the amine characterized by the usual tests. A water-soluble, non-volatile amine may also be converted to an arylsulfonyl derivative and separated from the organic acid (which is the other product of hydrolysis) by taking advantage of solubility behavior or differences in volatility.

Many substituted amides are hydrolyzed more easily by refluxing them with 20% sulfuric acid.

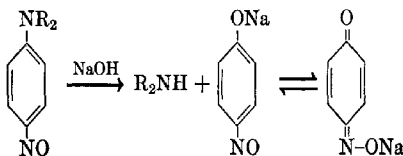


The acid if volatile may be separated by distillation or removed by filtration if it is insoluble in water. The amine may be liberated by the addition of alkali and characterized by conversion to its arylsulfonyl derivative.

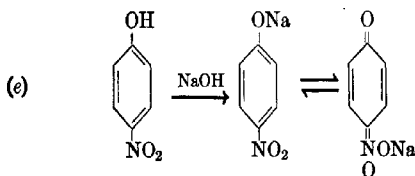
Nitriles, particularly cyanohydrins, are frequently hydrolyzed by acids. Treatment with 90 to 95% sulfuric acid or concentrated hydrochloric acid at temperatures ranging from 10 to 50° converts nitriles to amides. Amides may be hydrolyzed further by diluting the mixture with water and refluxing for ½ hour to 2 hours.



Aryl amines with nitro groups *ortho* or *para* to the amino group are hydrolyzed to the corresponding nitrophenols and ammonia or amines by the action of hot alkalies. The nitroso group resembles the nitro group in its labilizing effect on groups *ortho* or *para* to it. For example, *p*-nitrosodialkylanilines are hydrolyzed by alkalies to the secondary amines and the sodium salt of *p*-nitrosophenol (benzoquinone monoxime).



Nitro Compounds



To 5 ml. of 20% sodium hydroxide solution add 3 ml. of ethanol and a drop of nitrobenzene, and shake vigorously. Compare the color of the solution with that produced by a drop of nitrobenzene and 5 ml. of water plus 3 ml. of ethanol. Repeat the test with *p*-nitrophenol and *p*-nitroaniline.

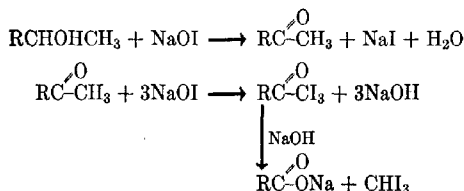
The exact cause of the change in color of a nitro compound has not been established definitely, but the above tautomerization to a quinoid ring is one explanation that has been advanced.

Dissolve 0.1 g. of *m*-dinitrobenzene in 10 ml. of acetone, and add 2 to 3 ml. of 10% sodium hydroxide solution, with shaking. Note the color produced. Try the test with nitrobenzene.

Discussion. Mononitro compounds give no color (or a very light yellow) with these reagents. If two nitro groups are present a bluish-purple color develops; the presence of three nitro groups produces a blood-red color. The presence of an amino, substituted amino, or hydroxyl group in the molecule inhibits the formation of the characteristic red and purple colors.¹

EXPERIMENT 29

Sodium Hypiodide. The Iodoform Test



Apply the following test to: (a) isopropyl alcohol; (b) acetone; (c) ethyl acetate; (d) ethyl acetoacetate; (e) acetophenone; (f) pure methanol.²

Place 4 drops of the liquid (0.1 g. of the solid) to be tested in a test tube (15 mm. wide). Add 5 ml. of dioxane, and shake until all the sample has gone into solution. Add 1 ml. of 10% sodium hydroxide solution, and then iodine-potassium iodide solution, with shaking, until a slight excess yields a definite dark color of

¹ Bost and Nicholson, *Ind. Eng. Chem., Anal. Ed.*, **7**, 190 (1935).

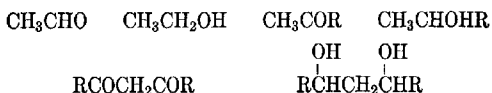
² Commercial methanol frequently gives a positive test owing to the presence of impurities.

iodine.¹ If less than 2 ml. of the iodine solution is decolorized, place the test tube in a water bath maintained at a temperature of 60°. If the slight excess of iodine already present is decolorized, continue the addition of iodine solution (keeping the dioxane solution at 60°), with shaking, until a slight excess of iodine solution again yields a definite dark color. The addition of iodine is continued until the dark color is not discharged by 2 minutes' heating at 60°. This excess of iodine is removed by the addition of a few drops of 10% sodium hydroxide solution, with shaking. Now fill the test tube with water and allow to stand for 15 minutes. If the compound is a solid it is advisable to collect the iodoform on a filter and determine its melting point; this should be 119–121°. If the iodoform is reddish in color, dissolve in 3 to 4 ml. of dioxane, add 1 ml. of 10% sodium hydroxide solution, and shake until only a light lemon color remains. Dilute with water and filter.

Reagent. The iodine-potassium iodide solution is made by adding 200 g. of potassium iodide and 100 g. of iodine to 800 ml. of distilled water and stirring until solution is complete.

Discussion. This test is positive for compounds that contain the grouping $\text{CH}_3\text{CO}-$, $\text{CH}_2\text{ICO}-$, or $\text{CHI}_2\text{CO}-$ when joined to a hydrogen atom or to a carbon atom which does not carry active hydrogen atoms or groups which provide an excessive amount of steric hindrance. The test will, of course, be positive also for any compound that reacts with the reagent to give a derivative containing one of the requisite groupings. Conversely, compounds that contain one of the requisite groupings will not give iodoform if that grouping is destroyed by the hydrolytic action of the reagent before iodination is complete.

Following are the principal types of compounds that give the test.



(R = any alkyl or aryl radical except a di-*ortho*-substituted aryl radical.)

¹ The iodine-potassium iodide solution must be added until a slight excess yields a dark color, because a few compounds give a yellow color on treatment with hypiodite. If dilution with water takes place here, no iodoform is obtained.

The test is negative for compounds of the following types.



In such compounds the acetyl group is cleaved by the reagent to acetic acid which resists iodination.¹

A modified reagent² has been suggested for distinguishing methyl ketones from methyl carbinols. It consists of a solution of 1 g. of potassium cyanide, 4 g. of iodine, and 6 ml. of concentrated ammonium hydroxide solution in 50 ml. of water. This reagent produces iodoform from methyl ketones but not from methyl carbinols.

EXPERIMENT 30

Sodium Iodide in Acetone



To 1 ml. of the acetone solution of sodium iodide in a test tube add 2 drops of the compound whose elementary analysis showed the presence of chlorine or bromine. If the compound is a solid, dissolve about 0.1 g. in the smallest possible volume of acetone, and add the solution to the reagent. Shake the test tube, and allow the solution to stand at room temperature for 3 minutes. Note whether a precipitate is formed and also whether the solution turns reddish-brown (owing to the liberation of free iodine). If no change occurs at room temperature, place the test tube in a beaker of water at 50°. At the end of 6 minutes, cool to room temperature and note whether a reaction has occurred. Try this test on: (a) *n*-butyl bromide; (b) *sec*-butyl bromide; (c) *tert*-butyl chloride; (d) ethylene bromide; (e) benzyl chloride; (f) benzoyl chloride; (g) benzenesulfonyl chloride; (h) α -chloroacetophenone.

Reagent. Fifteen grams of sodium iodide is dissolved in 100 ml. of pure acetone. The solution, colorless at first, becomes a pale lemon yellow. It should be kept in a dark bottle and should be discarded as soon as a definite red-brown color develops.

¹ For a general discussion of this test see Fuson and Bull, *Chem. Revs.*, **15**, 275 (1934).

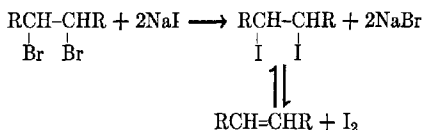
² Rothlin, *Arch. escuela farm. fac. ci. med. Córdoba [R.A.] Secc. ci.*, **1939**, No. 10, p. 1; *C. A.*, **35**, 5091 (1941).

Discussion. This test depends on the fact that sodium chloride and bromide are only very slightly soluble in acetone. It is based ¹ on an investigation of the relationship of structure to the reaction rates of a large number of halogen compounds,² and its value lies in the fact that numerous studies ^{3,4} indicate that the reaction follows a single mechanism, viz., a bimolecular anionic attack by the iodide ion on the carbon carrying the chlorine or bromine atom. For this reason, primary halides are more reactive than secondary halides toward the sodium iodide reagent. Tertiary halides react slowest—an order of reactivity which is just the reverse of that observed with ethanolic silver nitrate, which may exert its effect on organic halides by several different mechanisms.⁴

With sodium iodide, primary bromides give a precipitate of sodium bromide within 3 minutes at 25°, whereas the chlorides give no precipitate and must be heated to 50° in order to effect a reaction. Secondary and tertiary bromides react at 50°, but the tertiary chlorides fail to react within the time specified. Tertiary chlorides will react if the test solutions are allowed to stand for a day or two.

Acid chlorides and bromides, allylic chlorides and bromides, and α -halo ketones, esters, amides, and nitriles are highly reactive and give a precipitate of sodium halide at 25° within 3 minutes. Vinyl and aryl halides are inert.

1,2-Dichloro and 1,2-dibromo compounds may be detected by the sodium iodide reagent since they not only give a precipitate of sodium chloride or bromide but also liberate free iodine.



¹ Douglas M. Bowen, private communication.

² Conant and Kirner, *J. Am. Chem. Soc.*, **46**, 232 (1924); Conant and Hussey, *ibid.*, **47**, 476, 488 (1925).

³ Gilman, *Organic Chemistry*, pp. 273, 1053, 1864, John Wiley & Sons, New York, 1943.

⁴ Hammett, *Physical Organic Chemistry*, Chapter VI, McGraw-Hill New York, 1940.

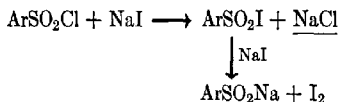
A comparison of ethylene halides gave the following results:

	Ppt. at 25°	
$\text{BrCH}_2\text{CH}_2\text{Br}$	1.5 min.	
$\text{BrCH}_2\text{CH}_2\text{Cl}$	3 min.	
$\text{ClCH}_2\text{CH}_2\text{Cl}$	None	(Ppt. at 50° in 2.5 min.)

Alicyclic halides, such as cyclohexyl chloride and bromide, bornyl chloride, and similar compounds fail to react with sodium iodide at 50° within 6 minutes. Simple polychloro compounds with the halogens on a single carbon atom, such as chloroform, carbon tetrachloride, and trichloroacetic acid, fail to react. However, benzal chloride and benzotrichloride are reactive because of the allylic system present.

Polybromo compounds such as bromoform and *s*-tetrabromoethane do react with sodium iodide at 50° to give a precipitate and liberate iodine. Carbon tetrabromide reacts at 25°.

Sulfonyl chlorides give an immediate precipitate and also liberate free iodine. Presumably the iodine is formed by the action of sodium iodide on the sulfonyl iodide.



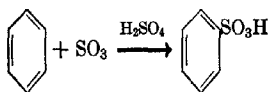
Alkyl sulfonates also react, producing the corresponding sodium sulfonates as precipitates.



This reaction must be kept in mind in the event that one of the groups in the sulfonic ester contains halogen.

EXPERIMENT 31

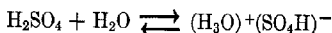
Sulfuric Acid (Fuming)



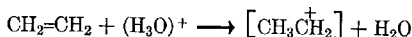
In a clean, dry test tube place 2 ml. of 20% fuming sulfuric acid and add 1 ml. of cyclohexane. Shake the mixture vigorously and

allow it to stand for a few minutes. Note whether solution has been effected. Repeat the experiment using: (a) benzene; (b) bromobenzene; (c) ethylene bromide.

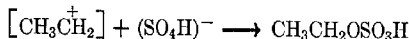
Discussion. Ordinary concentrated sulfuric acid reacts with ethylene to form ethyl hydrogen sulfate, but pure sulfuric acid converts the olefin into isethionic acid. Studies of the mechanism of addition reactions of olefins indicate that such reactions occur in steps. The first step involves combination of the olefin with the cation present. Since ordinary sulfuric acid contains about 5% of water, it dissociates to some extent as follows.



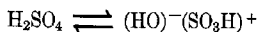
The first reaction occurs between the olefin and the hydronium ion.



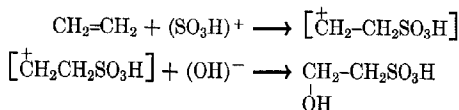
The second step occurs very rapidly and is the combination of the carbonium ion with the anion present to produce ethyl hydrogen sulfate.



Pure sulfuric acid acts as if it dissociated into hydroxyl ion and the sulfonate ion.

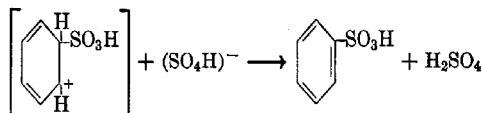
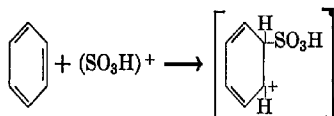
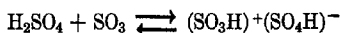


The stepwise reactions with ethylene are

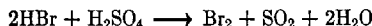
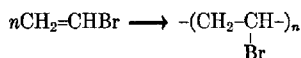
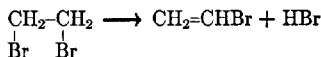


Substitution in aromatic hydrocarbons may also be a stepwise process, and it involves the same initial stage; the second step, however, consists in the removal of a proton by the anion in order to establish the conjugated aromatic system.¹ Sulfonation with fuming sulfuric acid appears to take the following course.

¹ Price, *Mechanisms of Reactions at Carbon-Carbon Double Bonds*, pp. 42-43, Interscience Publishers, Inc., New York (1946).



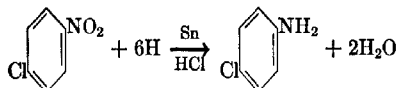
The action of fuming sulfuric acid on 1,2-dihalogen compounds is complex. The mixture turns dark, and some free halogen is liberated. It seems probable that loss of hydrogen halide occurs followed by polymerization of the vinyl halide. For example, ethylene bromide probably gives rise to the following changes.



Note that this test is useful only for compounds in solubility Class I. Why? Write equations for the reactions involved. Compare the products of this reaction with those formed in your solubility test with concentrated sulfuric acid and an olefin such as 1-hexene.

EXPERIMENT 32

Tin and Hydrochloric Acid



Add 1 g. of *p*-chloronitrobenzene to 2 g. of granulated tin in a small flask. Connect the flask to a reflux condenser, and add in

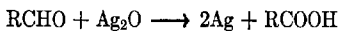
small portions 20 ml. of 10% hydrochloric acid, with vigorous shaking after each addition. Finally warm the mixture on the steam bath for 10 minutes. Decant the solution while it is still hot into 10 ml. of water, and add sufficient 40% sodium hydroxide solution to dissolve the tin hydroxide. Extract the solution several times with 10-ml. portions of ether. Dry the ether extract, and distil the ether. Test the solubility of the residue in dilute hydrochloric acid, and apply the Hinsberg test or the tests of Experiments 19 and 20 to it.

Discussion. The above reduction procedure is applicable not only to nitro compounds but also to azoxy, azo, and hydrazo compounds. Nitriles may also be reduced by the same general method but require longer treatment. With very insoluble nitro compounds the addition of 5 ml. of ethanol will hasten the reduction.

How is it possible to determine when the above reduction is complete? Show by a diagram the primary and secondary reduction products of nitrobenzene, and indicate the reducing agents used to obtain them.

EXPERIMENT 33

Tollens' Reagent



Prepare Tollens' reagent according to the directions below, and test its reaction with the following: (a) formalin; (b) acetone; (c) benzaldehyde; (d) glucose; (e) hydroquinone; (f) *p*-aminophenol.

Reagent. In a thoroughly clean test tube place 2 ml. of a 5% solution of silver nitrate, and add a drop of dilute sodium hydroxide solution (10%). Add a very dilute solution of ammonia (about 2%) drop by drop, with constant shaking, until the precipitate of silver oxide just dissolves. In order to obtain a sensitive reagent it is necessary to avoid a large excess of ammonia.

This reagent should be prepared just before use and should not be stored, since the solution decomposes on standing and deposits a highly explosive precipitate. If no reaction takes place in the cold the solution should be warmed slightly.

Would the presence of a reactive halogen atom interfere with this test?

EXPERIMENT 34

Volatility with Steam

Duclaux Constants for Volatile Aliphatic Acids

This test is useful for low-molecular-weight unsubstituted aliphatic acids containing from one to six carbon atoms. It is also valuable for characterizing esters of such acids, since the acids may be obtained from them by hydrolysis.

Procedure. Three grams of the acid is dissolved in 150 ml. of distilled water, and the solution is mixed thoroughly. Ten milliliters of the solution is removed by means of a pipet and is titrated against 0.1 *N* sodium hydroxide solution, phenolphthalein being used as the indicator. Then 100 ml. of the solution is placed in a 250- to 300-ml. distilling flask, and a few pieces of porous plate are added. A thermometer should not be used, but the top of the distilling flask should be closed with a clean rubber stopper. The flask is connected to a short water-cooled condenser by means of a rubber stopper in such a way that the side arm of the distilling flask extends well into the narrow portion of the condenser tube. The apparatus should be set up so that the condenser makes about a 45° angle with the desk top. The distilling flask is heated so that drops come from the end of the condenser at a constant rate. The distillation should not be so rapid that a steady stream flows from the condenser or so slow that there is an appreciable time interval between drops. Three 10-ml. fractions (A, B, C) are collected by means of a 10-ml. graduate. Each fraction is titrated separately with more of the 0.1 *N* sodium hydroxide solution used originally. The results are expressed as per cent acidity of the 100 ml. used.

Duclaux number =

$$\frac{\text{Volume of alkali (ml.) for 10-ml. fraction} \times 100}{\text{Volume of alkali (ml.) for original 10 ml.} \times 10}$$

The Duclaux numbers for the common aliphatic acids are given in Table XVI.

Discussion. An exactly standardized sodium hydroxide solution is unnecessary but it should be about 0.1 *N*. This procedure

TABLE XVI
DUCLAUX NUMBERS

Acid	Fraction A	Fraction B	Fraction C
Formic	3.95	4.40	4.55
Acetic	6.8	7.1	7.4
Propionic	11.9	11.7	11.3
<i>n</i> -Butyric	17.9	15.9	14.6
Isobutyric	25.0	20.9	16.0
<i>n</i> -Valeric	24.5	20.6	17.0
Isovaleric	28.7	23.1	16.8
<i>n</i> -Caproic	33.0	24.0	19.0

is an empirical one, and the values are only relative. They are an index of the relative volatility of the acid and water at the concentration stated. The volume of the graduate should be checked against that of the 10-ml. pipet.

Questions

1. What is an azeotropic mixture?
2. Formic acid (77.5%) and water (22.5%) constitute an azeotropic mixture. If this were the concentration used in the distillation, what would be the Duclaux numbers? Suppose that a solution containing 90% formic acid were used; what could you say concerning the relative Duclaux numbers for fractions A, B, and C?
3. Acetic acid (28%) and toluene (72%) constitute an azeotropic mixture. How could such a mixture be separated?
4. Can you suggest any possible explanation, from a structural point of view, of the fact that the higher acids do not form azeotropic mixtures with water? Why are the Duclaux numbers for fraction A for these acids higher than those for fractions B and C?
5. Ethyl acetate was saponified by treatment with sodium hydroxide solution. Phosphoric acid was added, and a portion of the solution was distilled. When Duclaux numbers were determined for this distillate they failed to check the values for acetic acid. Explain. How should the procedure have been modified?

EXPERIMENT 35

Water-ether Partition Coefficients for Organic Acids¹

Dissolve about 2 g. of the unknown acid in 50 ml. of distilled water, and titrate exactly 10 ml. of the solution (measured by a pipet or buret) with a previously standardized solution of sodium

¹ Dermer and Dermer, *J. Am. Chem. Soc.*, **65**, 1653 (1943).

hydroxide (about 0.1 *N*), phenolphthalein being used as the indicator. Calculate the exact normality of the original acid solution, and dilute a portion of it with enough distilled water to make the solution 0.100 *N* (± 0.005).

Transfer exactly 50 ml. of this 0.1 *N* solution by means of a pipet to a clean, dry 200-ml. separatory funnel, and add 50 ml. of water-saturated ether (free from alcohol), also by means of a pipet. Shake the mixture for 5 minutes, and allow to stand a few minutes to permit the layers to separate. Drain the lower, aqueous layer into a clean flask, taking care to leave a few milliliters in the separatory funnel. By means of a pipet remove 20 ml. of the aqueous layer and titrate it with the 0.1 *N* alkali, phenolphthalein being used as the indicator. Then transfer a 20-ml. portion of the ether layer by means of a pipet to a flask containing 20 ml. of distilled water and titrate with the 0.1 *N* alkali. From these values calculate the ratio of the concentration in water to that in ether.

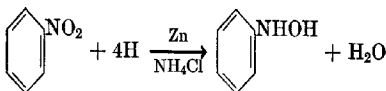
Values for C_w/C_e for some common acids are as follows: benzenesulfonic, 300; *d*-camphorsulfonic, 300; *d*-tartaric, 280; acetyl-glycine, 150; citric, 150; glycine, 120; mesotartaric, 120; *l*-malic, 75; *dl*-malic, 52; sulfosalicylic, 36; diglycolic, 35; glycolic, 35; oxamic, 31; oxalic, 25; tricarballic, 20; lactic, 14; malonic, 12.0; maleic, 10.9; hydracrylic, 10.0; potassium acid phthalate, 8.1; succinic, 7.8; methoxyacetic, 5.7; levulinic, 4.4; α -hydroxyisobutyric, 4.4; aconitic, 4.2; glutaric, 3.7; cyanoacetic, 3.3; itaconic, 3.0; formic, 2.8; ethoxyacetic, 2.2; acetic, 2.1; adipic, 1.9; fumaric, 0.80; phthalic, 0.79; pimelic, 0.73; β -bromopropionic, 0.70; propionic, 0.63; *dl*-mandelic, 0.50; acrylic, 0.49; chloroacetic, 0.46; bromoacetic, 0.31; furoic, 0.26; crotonic, 0.25; α,β -dibromopropionic, 0.24; trichloroacetic, 0.24; β -chloropropionic, 0.24; butyric, 0.21; valeric, 0.20; isobutyric, 0.19; dichloroacetic, 0.18; benzoylformic, 0.16; α -chloropropionic, 0.14; α -bromopropionic, 0.110; isovaleric, 0.108; β -iodopropionic, 0.103; *dl*-methylethylacetic, 0.092; β -chlorobutyric, 0.087; trimethylacetic, 0.077; isocaproic, 0.058; α -bromobutyric, 0.056; phenylacetic, 0.047.

Discussion. This solvent-partition method has some advantages over the Duclaux method. In particular, it is not limited to volatile acids and hence has wider applicability. The values for closely related acids, however, are too near to each other for identification (cf. butyric [0.21], valeric [0.20], and isobutyric [0.19]).

The precision of measurement of these ratios is about $\pm 2\%$ of their own values in the region where $C_w/C_e = 1$, but decreases to $\pm 4\%$ when C_w/C_e is as large as 35 or as small as 0.05. For still higher values of the ratio the precision is much poorer (± 10 – 20%).

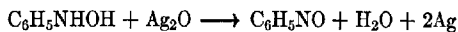
EXPERIMENT 36

Zinc and Ammonium Chloride



Dissolve 0.5 ml. of nitrobenzene in 10 ml. of 50% ethanol, and add 0.5 g. of ammonium chloride and 0.5 g. of zinc dust. Shake, and heat to boiling. Allow to stand 5 minutes, filter, and test the action of the filtrate on Tollens' reagent.

This test depends on the reduction of the unknown to a hydrazine, a hydroxylamine, or an aminophenol; all these compounds are oxidized by Tollens' reagent, which is reduced to metallic silver.



This test cannot be applied if the original compound reduces Tollens' reagent.

EXERCISES

I. Write equations for the reactions which occur in the following tests. Assume that they are carried out under the experimental conditions specified for the classification reagents. Reactions may be written as taking place in steps when this is desirable.

1. Vanillin + hydriodic acid.
2. Crotonic acid + potassium permanganate solution.
3. Acetophenone + hydroxylamine hydrochloride.
4. *n*-Butanol + iodic acid.
5. *N*-Ethylphthalimide + hot sodium hydroxide solution.
6. *N*-Methylaniline + nickel chloride + carbon disulfide + ammonium hydroxide.
7. Ethanolamine + sodium nitrite + hydrochloric acid.
8. *o*-Dichlorobenzene + fuming sulfuric acid.
9. DDT + hot sodium hydroxide solution.
10. 2,3-Dibromopentane + sodium iodide solution.
11. 2-Octanol + sodium hypiodite solution.

12. Benzyl iodide + alcoholic silver nitrate.
13. α -Naphthol + bromine water.
14. Alanine + benzenesulfonyl chloride + sodium hydroxide.
15. β -Diethylaminoethanol + acetyl chloride.

II. Arrange the following compounds in the approximate order of decreasing reactivity of the halogen atom to alcoholic silver nitrate.

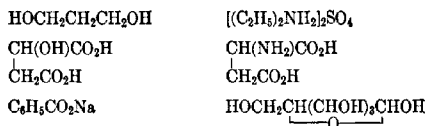
1. $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ (*p*) $\text{CH}_2\text{C}_6\text{H}_4\text{Cl}$ $\text{C}_6\text{H}_5\text{COCl}$ $(\text{C}_6\text{H}_5)_3\text{CCl}$
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ $(\text{CH}_3)_2\text{CHCl}$.
2. $\text{BrCH}_2\text{CO}_2\text{H}$ $(\text{CH}_3)_2\text{CHBr}$ $\text{C}_6\text{H}_5\text{NH}_2\text{Cl}$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$.
3. $\text{CH}_3\text{CHBrCH}=\text{CH}_2$ $\text{C}_6\text{H}_5\text{Br}$ $\text{C}_6\text{H}_5\text{COCH}_2\text{Cl}$
 $\text{BrCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ $\text{ClCH}_2\text{CH}_2\text{CH}=\text{CH}_2$.

III. What would be the approximate order of reactivity of the halogen atoms in the above compounds if an acetone solution of sodium iodide was the reagent?

IV. Select a classification test which could be used to distinguish between the following pairs of compounds.

1. (*p*) $\text{ClC}_6\text{H}_4\text{COCH}_3$ and $\text{C}_6\text{H}_5\text{COCH}_2\text{Cl}$.
2. $(\text{C}_2\text{H}_5)_3\text{COH}$ and *n*- $\text{C}_4\text{H}_9\text{OH}$.
3. $\text{C}_2\text{H}_5\text{CHO}$ and CH_3COCH_3 .
4. $\text{HO}(\text{CH}_2)_4\text{OH}$ and $\text{CH}_3\text{CH}_2\text{CH}-\text{CH}_2$
 $\begin{array}{c} \text{OH} \quad \text{OH} \\ | \quad | \end{array}$
5. Glucose and fructose.
6. Sucrose and lactose.
7. $\text{CH}_3\text{OCH}_2\text{CO}_2\text{H}$ and $\text{HOCH}_2\text{CO}_2\text{CH}_3$.
8. Cyclohexene and anisole.
9. $(\text{CH}_3)_2\text{C}(\text{CO}_2\text{CH}_3)_2$ and $\text{CH}_2(\text{CO}_2\text{C}_2\text{H}_5)_2$.
10. $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ and (*p*) $\text{CH}_2\text{C}_6\text{H}_4\text{NH}_2$.

V. Suppose that the labels were lost from six bottles known to contain the following six compounds:



Select a sequence of tests (do not use melting points or boiling points) which could be used to relabel the bottles quickly and correctly. What is the smallest number of tests that would suffice?

VI. A compound may be any one of the following:

- | | |
|---------------------------------|---------------------------|
| 1. 2-Heptanol. | 6. Ethyl phenyl ether. |
| 2. Benzyl methyl ketone. | 7. Ethyl cinnamate. |
| 3. Ethyl <i>n</i> -valerate. | 8. Benzil. |
| 4. <i>n</i> -Butyric anhydride. | 9. <i>n</i> -Hexaldehyde. |
| 5. 1,1-Diethoxypropane. | 10. Benzalacetone. |

A. The action of the following reagents was tried on each of the above compounds. State which reagents resulted in positive tests and which negative. Write equations for the positive tests.

- (a) Hot dilute sodium hydroxide solution.
- (b) Hydroxylamine hydrochloride.
- (c) Sodium hypoiodite.
- (d) Dilute potassium permanganate.

B. Suppose that each of the above reagents gave a negative test. What possibilities are left for consideration, and how could one differentiate between them?

VII. The following observations are frequently made in the laboratory. In each case state the deductions which may be drawn as to the nature of the compound being studied.

- (a) A water solution of an ether-insoluble compound reacts acid to litmus.
- (b) A compound in Class A_1 decolorizes a dilute permanganate solution in the cold.
- (c) A Class M compound containing nitrogen dissolves completely in dilute, boiling sodium hydroxide solution.
- (d) A Class N_1 compound gives a precipitate when shaken with a saturated solution of sodium bisulfite.
- (e) A Class I compound is insoluble in fuming sulfuric acid.
- (f) A compound in Class S_1 reacts with acetyl chloride and gives a yellow precipitate when treated with a solution of sodium hypoiodite.
- (g) The action of nitrous acid on a Class B compound converts it into a green solid. The original compound, however, does not react with acetyl chloride.
- (h) A hydrocarbon yields a sodium derivative.
- (i) A compound containing only carbon, hydrogen, and oxygen yields two products when treated with hot alkali.
- (j) A Class A_1 compound is changed to a Class N_1 compound by heating.
- (k) A Class A_2 compound is converted into a Class S_1 -B compound by reduction, and into a Class N_1 compound by hydrolysis.
- (l) A Class B-M compound gives a Class A_2 compound when treated with *p*-toluenesulfonyl chloride, and a Class A_1 compound when treated with nitrous acid.
- (m) A Class $A_1(B)$ compound gave a clear solution with benzenesulfonyl chloride and alkali. Addition of acid gave a precipitate. Treatment of the parent compound with hydrochloric acid and sodium nitrite failed to liberate nitrogen even when the reaction mixture was warmed.
- (n) A compound in Class S_2 left a residue on ignition. An aqueous solution of this residue was alkaline to litmus.
- (o) A Class S_1 compound was acid to moist litmus. It reduced permanganate but did not decolorize bromine in carbon tetrachloride. It did decolorize bromine water.
- (p) A Class B compound reacted with benzenesulfonyl chloride and alkali to give a clear solution. Careful neutralization of this solution produced a precipitate which was not the original compound but which dissolved in an excess of dilute hydrochloric acid.

CHAPTER VIII

THE PREPARATION OF DERIVATIVES

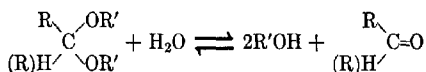
This chapter deals with the selection and preparation of derivatives, a subject which was outlined briefly in Chapter II. The derivatives are grouped according to the classes of compounds for which they are used, the classes in turn being arranged alphabetically.

The directions for preparing derivatives in this chapter are designated as *procedures*. The classification reactions discussed in Chapter VII may frequently be used for making derivatives; directions for these are referred to as *experiments*.

ACETALS

(Listed on p. 219)

Acetals are identified by reference to the alcohol and the aldehyde or ketone which they yield when hydrolyzed. The hydrolysis is accomplished by heating the acetals with dilute acids; under these conditions the following reaction occurs.



Low-molecular-weight acetals are readily hydrolyzed by refluxing with 1 to 2% hydrochloric acid for 3 to 5 minutes. Higher-molecular-weight acetals require a longer time (30 to 60 minutes). The hydrolysis of acetals of water-insoluble alcohols and aldehydes or ketones may be facilitated by using a 50% solution of dioxane as the solvent.

The exact procedure to be followed is dependent on the hydrolysis products. If the alcohol and carbonyl compound are both water soluble the hydrolysis mixture is made neutral to litmus and divided in half. One portion is used for the characterization

of the aldehyde or ketone by the preparation of a suitable derivative. Semicarbazones (Procedure 13), phenylhydrazones (Experiment 23, p. 116), and *p*-nitrophenylhydrazones (Procedure 14) will be found useful. The second portion of the hydrolysis mixture is treated with benzoyl chloride according to the Schotten-Baumann method (Experiment 1e, p. 88). This converts the alcohol to the corresponding alkyl benzoate, which is separated and hydrolyzed by Method A of Experiment 28 (p. 130). The alcohol is then characterized by one of the methods described on page 159.

If one of the hydrolysis products is insoluble in the reaction mixture it is separated and characterized first. The product in the aqueous solution is then treated by either of the methods mentioned above.

If both the alcohol and carbonyl compound are insoluble, they are separated from the aqueous layer. In the event that one of the products is an aldehyde or an aliphatic methyl ketone it may be separated from the alcohol by means of its bisulfite compound (Experiment 27, p. 127). Sometimes fractional distillation may be used to separate the alcohol and carbonyl compound.

ACID HALIDES AND ANHYDRIDES

(Listed on p. 220)

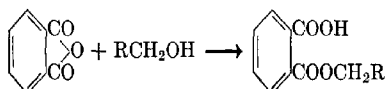
Acid halides and anhydrides are identified most often by reference to anilides, which they form when treated with aniline (Experiment 1b, p. 87). If the corresponding amide is water insoluble, the acid halide or anhydride may be treated with concentrated aqueous ammonia in order to produce the amide.

Acid chlorides of dibasic acids react with an excess of aniline at ordinary temperatures to produce the dianilides. If an anhydride of a dibasic acid is heated with aniline the *N*-phenylimide may be produced. This frequently serves as a derivative.

Hydrolysis converts acid halides or anhydrides into the corresponding acids. If the acid is a solid, it frequently will serve as a derivative. In other cases the acid halide or anhydride may be hydrolyzed with dilute alkali, the solution neutralized with hydrochloric acid (phenolphthalein) and evaporated. The mixture of the sodium salt of the acid and sodium chloride may be used for preparing solid esters such as those described under acids on page 154.

Acid halides and anhydrides react with alcohols and phenols to produce esters (Experiment 1*d*, p. 87) which may serve for identification. The alcohol or phenol must be so chosen that the product will be a solid.

Alcohols react with acid chlorides of dibasic acids to produce normal esters, but with an anhydride of a dibasic acid the acid ester is the chief product. Phthalic anhydride combines with alcohols to give alkyl hydrogen phthalates.



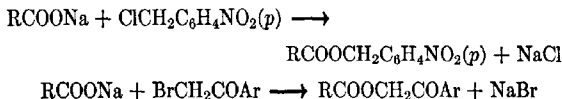
The diester is produced only if a catalyst is used and an excess of the alcohol is present.

ACIDS

(Listed on p. 222)

The Duclaux constants (Table XVI, p. 147) furnish one means of identification of those saturated monobasic acids having fewer than seven carbon atoms. It is unsuitable for *n*-valeric and isobutyric acid because the constants for these two acids lie close together. Neutralization equivalents of acids (p. 128) and partition coefficients (p. 147) are also very valuable. It is usually desirable and frequently necessary to confirm the identification of the acids by means of solid derivatives.

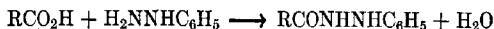
Solid esters furnish a useful means for characterizing the acids. Some methyl esters are solid but in most cases one must use *p*-nitrobenzyl, phenacyl, *p*-chlorophenacyl, *p*-bromophenacyl, or *p*-phenylphenacyl esters. These are prepared by treating the salts of the acids with the corresponding halide (Procedure 1).



This method is particularly advantageous because it does not require an anhydrous sample of the acid.

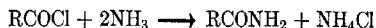
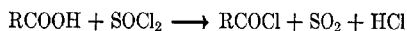
The reaction products of phenylhydrazine and acids are also good derivatives. At the boiling point (243°) of phenylhydrazine,

simple unsubstituted aliphatic mono- and dibasic acids form phenylhydrazides (Procedure 4).



Salts of phenylhydrazine are obtained from sulfonic acids, α -chloro aliphatic acids, and aliphatic dibasic acids when warmed with a benzene solution of phenylhydrazine.

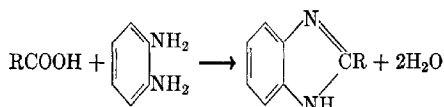
Acids may be converted to amides by treatment with thionyl chloride and then with ammonia.



This method is particularly suitable if the amide is insoluble in water; it may be made by adding the acid chloride to concentrated aqueous ammonia (Procedure 2).

Anilides, toluides, and *p*-bromoanilides are excellent derivatives because of the ease with which they may be made and purified. They may be made either from the free acid or from its salt (Procedure 3).

The dimethylamides and the diamides derived from *p,p'*-diaminodiphenylmethane have found application also as derivatives. Acids condense with *o*-phenylenediamine to produce 2-alkylbenzimidazoles, which are useful derivatives.



Salts derived from organic acids and strongly basic amines such as benzylamine, α -phenylethylamine, or piperazine are also good derivatives.

Salts of Acids

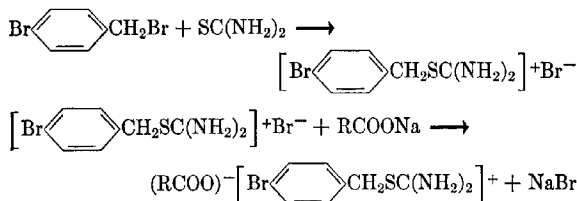
Addition of a strong mineral acid to the metal salt of a carboxylic acid liberates the free organic acid.



The free organic acid may be isolated by distillation, extraction, or filtration. Since the metal salts melt only at very high temperatures and usually decompose, it is necessary to use the physical

constants of the acid to prepare the list of possibilities. The acid may then be converted to a suitable derivative, or the salt may be used directly for the preparation of the anilide, toluides (Procedure 3), or *p*-nitrobenzyl or *p*-bromophenacyl ester (Procedure 1).

p-Bromobenzylpseudothiuronium bromide, prepared by heating *p*-bromobenzyl bromide with thiourea, reacts with the sodium or potassium salts of carboxylic acids to yield the corresponding *p*-bromobenzylpseudothiuronium salts (Procedure 5).



Benzyl and *p*-chlorobenzylpseudothiuronium salts are made in a similar way. The salts form in nearly pure condition but possess melting points which are very close together.

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PROCEDURE 1

***p*-Nitrobenzyl, Phenacyl, *p*-Chlorophenacyl, *p*-Bromophenacyl, and *p*-Phenylphenacyl Esters**

One gram of the acid is added to 5 ml. of water in a small flask and is neutralized carefully with 10% sodium hydroxide solution. A few drops of the acid are added, the addition being continued until the solution is just acid to litmus. If the original acid is obtained as the sodium salt, 1 g. of the salt is dissolved in 5 to 10 ml. of water. If this solution is alkaline a drop or two of dilute hydrochloric acid is added. Ten milliliters of alcohol and 1 g. of the phenacyl bromide¹ are added; the mixture is then heated under reflux for 1 hour if the acid is monobasic, 2 hours if dibasic, and 3 hours if tribasic. Occasionally the addition of a few more milliliters of alcohol may be necessary if a solid separates during the refluxing. The solution is allowed to cool, and the precipitated ester is purified by recrystallization from alcohol.

In preparing derivatives with these reagents care must be taken that the original reaction mixture is not alkaline. Alkalies cause hydrolysis of the phenacyl halides to phenacyl alcohols. Also, *p*-bromophenacyl bromide should not be used if considerable amounts of sodium chloride are present in the sodium salt of the acid.² A special procedure must be followed to obtain substituted phenacyl formates.³

PROCEDURE 2

Amides from Acids

One gram of the acid is heated under reflux with 5 ml. of thionyl chloride for 15 to 30 minutes. The reaction mixture is poured into 15 ml. of ice-

¹ Caution! Phenacyl halides are lachrymatory.

² Pokras and Bernstein, *J. Am. Chem. Soc.*, **65**, 2096 (1943).

³ Kubota and Matsuura, *J. Inst. Polytech. Osaka*, **1**, 49 (1950).

cold, concentrated ammonia. The precipitated amide is collected on a filter and purified by recrystallization from water or dilute alcohol.

PROCEDURE 3

Anilides, *p*-Toluides, and *p*-Bromoanilides

A. One gram of the acid or its sodium salt is mixed with 2 ml. of thionyl chloride in a test tube, and the mixture is heated under a small reflux condenser for 30 minutes. The mixture is cooled, a solution of 1 to 2 g. of the amine (aniline, *p*-toluidine, or *p*-bromoaniline) in 30 ml. of benzene is added, and the mixture is warmed on the steam bath for 2 minutes. The benzene solution is decanted into a separatory funnel and washed successively with 2 ml. of water, 5 ml. of 5% hydrochloric acid, 5 ml. of 5% sodium hydroxide solution, and 2 ml. of water. The benzene is evaporated and the amide recrystallized from water or alcohol.

B. A mixture of 0.4 g. of the dry powdered sodium salt of the acid, 1 ml. of the arylamine, and 0.3 ml. of concentrated hydrochloric acid is placed in a test tube. The test tube is placed in an oil bath which is then heated, and the temperature is kept between 150° and 160° for 45 to 60 minutes. At the end of this time, the test tube is removed and the product purified by one of the following methods.

(a) If the acid under consideration has fewer than six carbon atoms, the crude product is boiled with 5 ml. of 95% alcohol and the solution decanted into 50 ml. of hot water. The resulting solution is evaporated to a volume of 10 to 12 ml. and cooled in an ice bath. The crystals are removed by filtration and recrystallized from a small amount of water or dilute alcohol.

(b) If the acid contains six or more carbon atoms, the crude reaction product is powdered and washed with 15 ml. of 5% hydrochloric acid and then with 15 ml. of cold water. The residue is boiled with 30 to 40 ml. of 50% alcohol, and the solution is filtered. The filtrate is chilled in an ice bath, and the crystals of the substituted amide are removed by filtration. The product may be recrystallized from dilute alcohol.

PROCEDURE 4

Phenylhydrazides and Phenylhydrazonium Salts

A. One gram of the acid is dissolved in 2 ml. of phenylhydrazine, and the solution is boiled gently for 30 minutes. The crystalline product that separates when the solution cools is isolated by suction filtration and washed with small quantities of benzene or ether until the crystals are white. When a large excess of phenylhydrazine is used, it is sometimes

necessary to dilute the mixture with benzene in order to bring about precipitation of the product. The derivatives of the lower monobasic acids are recrystallized from hot benzene, whereas those of the higher acids and dibasic acids are best recrystallized from alcohol or alcohol-water mixtures. The derivatives obtained from dibasic acids by this method are *bis-β*-phenylhydrazides.

B. One gram of the acid is mixed with 2 ml. of phenylhydrazine dissolved in 5 ml. of benzene. Sometimes a white solid precipitates immediately; it is recrystallized from alcohol. If no solid separates, the mixture is refluxed for 30 minutes, and the product that precipitates upon cooling is collected on a filter, washed with ether, and recrystallized from benzene or alcohol. Sulfonic acids, halogen-substituted aliphatic acids, and aliphatic dibasic acids yield salts by this procedure, whereas simple unsubstituted aliphatic acids give phenylhydrazides.

PROCEDURE 5

Benzyl-, *p*-Chlorobenzyl-, and *p*-Bromobenzylpseudothiuronium Salts

About 0.3 g. of the acid (or 0.5 g. of the sodium or potassium salt) is added to 3 or 4 ml. of water, a drop of phenolphthalein indicator solution is added, and the solution is neutralized by the dropwise addition of 5% sodium hydroxide solution. An excess of alkali must be avoided. If too much is added, dilute hydrochloric acid is added until the solution is just a pale pink. To this aqueous solution of the sodium salt is added a hot solution of 1 g. of the aralkylpseudothiuronium chloride or bromide in 10 ml. of 95% ethanol. The mixture is cooled, and the salt is collected on a filter. A few acids (e.g., formic) fail to precipitate, and part of the alcohol must be evaporated to obtain the salt.

These pseudothiuronium salts of organic acids separate in a state of high purity and usually do not require recrystallization. If necessary they may be recrystallized from a small amount of dioxane.

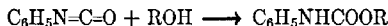
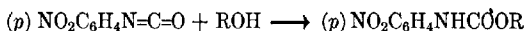
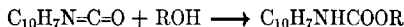
The melting points of many of these salts are close together, a large number of them melting within a narrow temperature range. Hence, it is always best to confirm the identification by some additional criterion such as Duclaux constant, partition coefficient, or neutralization equivalent.

ALCOHOLS

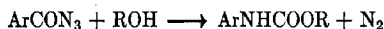
(Listed on p. 226)

The most general derivatives of primary and secondary alcohols are the α -naphthyl-, *p*-nitrophenyl-, and phenylurethans. These

are formed when the alcohol is treated with α -naphthyl, *p*-nitrophenyl, and phenyl isocyanate (Procedure 6), respectively.

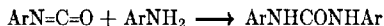


Urethans are also produced by treating alcohols with acid azides (Procedure 6D).



4-Iodobiphenylurethans, *o*- and *m*-nitrophenylurethans, 3,5-dinitrophenylurethans, 4-xenylurethans, *p*-anisylurethans, and *p*-bromophenylurethans have also been recommended for use in the characterization of alcohols.

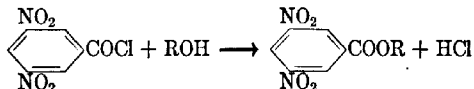
The presence of water as an impurity in the alcohol causes difficulty in obtaining urethans by either of these methods. Water hydrolyzes the isocyanates to give arylamines which combine with the excess reagent to produce disubstituted ureas.



The ureas are higher melting and less soluble than the corresponding urethans; and ureas, even in small amounts, make the isolation and purification of the urethans a matter of considerable difficulty. For this reason, this procedure is most useful for alcohols which are insoluble in water and, therefore, easily obtained in anhydrous condition.

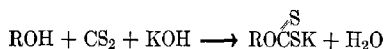
Urethans can be obtained from tertiary alcohols only with great difficulty. The isocyanates cause dehydration to occur with the formation of the olefin and diarylurea.

For water-soluble alcohols which are likely to contain traces of moisture the 3,5-dinitrobenzoates are generally more satisfactory as derivatives than the urethans. The 3,5-dinitrobenzoates are made by treating the alcohols with 3,5-dinitrobenzoyl chloride (Procedure 9).

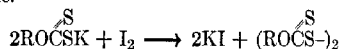


Double compounds of these alkyl 3,5-dinitrobenzoates with α -naphthylamine have also been found useful.

Other types of esters, such as the *p*-nitrobenzoates (Procedures 7A, 7B), *p*-nitrobenzyl phthalates, and 1-nitroanthraquinone-2-carboxylates have found application as derivatives. In the case of glycols and polyhydroxy compounds, the benzoates (Procedure 7) and acetates (Procedures 8A or 8B) may be used. The 3-nitrophthalates (Procedure 10) are valuable not only for the simple alcohols but also for the alkyl ethers of ethylene glycol (cellosolves) and diethylene glycol (carbitols). The xanthates are also suitable for the identification of primary and secondary alcohols.



They have been used for identifying the cellosolves and carbitols since the derivatives not only have definite decomposition points but also may be characterized by titration with a standard solution of iodine.

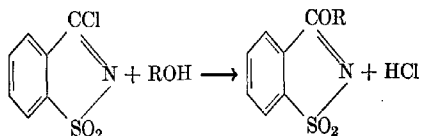


When treated with trityl chloride in the presence of pyridine, alcohols yield trityl ethers.

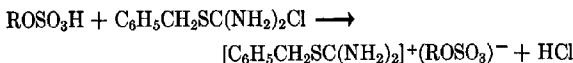


The trityl ethers are especially useful in the characterization of cellosolves, carbitols, and related glycols. These substituted alcohols also yield crystalline 3,4,5-triiodobenzoates.

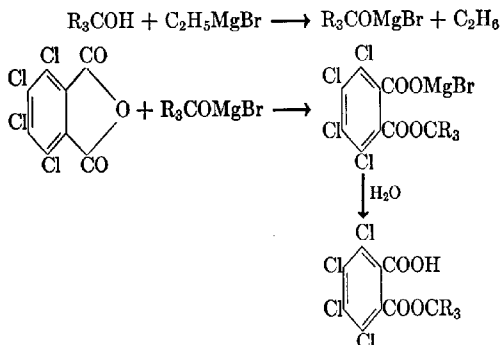
Pseudosaccharin chloride, made by the action of phosphorus pentachloride on saccharin, reacts with alcohols to produce *O*-alkylsaccharin derivatives which are useful in the identification of primary and secondary alcohols.



A number of primary and secondary alcohols are identified easily by conversion to alkyl hydrogen sulfates followed by formation of a salt with *S*-benzylthiuronium chloride (Procedure 11)



Tertiary alcohols are converted into chlorides by the action of acyl chlorides and are dehydrated by the action of anhydrides or isocyanates. Esters may be prepared in satisfactory yields, however, if the reaction is allowed to take place in the presence of a base or a metal which reacts with the hydrochloric acid as fast as it forms. Simple trialkylcarbinols may be converted into tetra-chlorophthalates by the following reactions:



These substituted phthalates may be characterized by their decomposition points and neutralization equivalents.

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PROCEDURE 6

Urethans

A. Phenyl- and α -Naphthylurethans. One gram of the anhydrous alcohol or phenol is placed in a test tube, and 0.5 ml. of phenyl isocyanate¹ or α -naphthyl isocyanate is added. If the reactant is a phenol, the reac-

¹ Caution! The isocyanates are lachrymatory.

tion should be catalyzed by the addition of 2-3 drops of anhydrous pyridine or triethylamine. If a spontaneous reaction does not take place the solution should be warmed on the steam bath for 5 minutes. It is then cooled in a beaker of ice, and the sides of the tube are scratched with a glass rod in order to induce crystallization. The urethan is purified by dissolving it in 5 ml. of petroleum ether or carbon tetrachloride, filtering the hot solution, and cooling the filtrate in an ice bath. The crystals are collected on a filter and dried on a clay plate; the melting point is then determined.

B. Diphenylurethans. One-half gram of the phenol is mixed with 0.5 g. of diphenylcarbonyl chloride, and the mixture is heated for a few minutes over a low flame. The product solidifies when the mixture is cooled in an ice bath and is purified by recrystallization from petroleum ether, carbon tetrachloride, or benzene.

C. *p*-Nitrophenylurethans. One-half gram of *p*-nitrophenyl isocyanate in 5 ml. of benzene is treated with 0.5 g. of alcohol. A spontaneous reaction takes place which is complete in about 5 minutes. The benzene is evaporated by means of a steam cone, and the residue is warmed with 10 ml. of carbon tetrachloride. The solution is filtered while hot, and the carbon tetrachloride is evaporated by means of a steam cone to a volume of 1 to 2 ml. When cooled this solution deposits the urethan, which is collected on a filter.

D. *p*-Nitrophenylurethans from Acid Azides. A mixture of 0.5 g. of *p*-nitrobenzazide, 1 g. of the phenol or alcohol, and 10 to 20 ml. of dry ligroin (B. P. 80-125°) is heated under reflux for 2 hours and allowed to cool; the crystals of the urethan are removed by filtration. Frequently the derivative separates in the pure state, but if necessary it may be recrystallized from ligroin, benzene, or ethyl acetate.

A similar procedure may be followed for the preparation of urethans from other substituted benzazides.

PROCEDURE 7

Benzoates and *p*-Nitrobenzoates

A. One milliliter of the alcohol is dissolved in 3 ml. of anhydrous pyridine, and 0.5 g. of benzoyl or *p*-nitrobenzoyl chloride is added. After the initial reaction has subsided the mixture is warmed over a low flame for a minute and poured, with vigorous stirring, into 10 ml. of water. The precipitate is allowed to settle, and the supernatant liquid is decanted. The residue is stirred thoroughly with 5 ml. of 5% sodium carbonate solution, removed by filtration, and purified by recrystallization from alcohol.

B. One milliliter of the alcohol, mixed with 0.5 g. of benzoyl or *p*-nitrobenzoyl chloride, is boiled over a low flame for a few minutes. The mixture is poured into water and purified as described above.

PROCEDURE 8

Acetates

A. Three grams of the anhydrous polyhydroxy compound is mixed with 1.5 g. of powdered fused sodium acetate and 15 ml. of acetic anhydride. The mixture is heated on the steam bath, with occasional shaking, for 2 hours. At the end of this time the warm solution is poured, with vigorous stirring, into 100 ml. of ice water. The mixture is allowed to stand, with occasional stirring, until the excess of acetic anhydride has been hydrolyzed. The crystals are removed by filtration, washed thoroughly with water, and purified by recrystallization from alcohol.

B. Two grams of the polyhydroxy compound is added to 20 ml. of anhydrous pyridine. Eight grams of acetic anhydride is added, with shaking, and after any initial reaction has subsided the solution is boiled for 3 to 5 minutes under a reflux condenser. The mixture is cooled and poured into 50 to 75 ml. of ice water. The acetyl derivative is removed by filtration, washed with cold 2% hydrochloric acid, and then washed with water. It is purified by recrystallization from alcohol.

PROCEDURE 9

3,5-Dinitrobenzoates

About 0.5 g. of 3,5-dinitrobenzoyl chloride is mixed with 2 ml. of the alcohol in a test tube and the mixture boiled gently for 5 minutes. Then 10 ml. of distilled water is added and the solution is cooled in an ice bath until the product solidifies. The precipitate is collected on a filter, washed with 10 ml. of 2% sodium carbonate solution, and recrystallized from 5 to 10 ml. of a mixture of ethyl alcohol and water of such composition that the ester will dissolve in the hot solution but will separate when the solution is cooled. After the crystals have been removed by filtration and dried on a porous plate the melting point is determined.

If 3,5-dinitrobenzoyl chloride is not available it may be made by mixing 0.5 g. of 3,5-dinitrobenzoic acid with 1 g. of phosphorus pentachloride in a test tube. The mixture is warmed gently to start the reaction. After the initial rapid reaction has subsided the mixture is heated for about 4 minutes at such a rate as to cause vigorous bubbling. While still liquid the mixture is poured on a watch glass, and the mass is allowed

to solidify. The material is transferred to a clean clay plate and rubbed with a spatula in order to remove phosphorus oxychloride. The residual acid chloride is used immediately for the preparation of the derivative as described above.

3,5-Dinitrobenzoates may be prepared also by the pyridine method described in Procedure 7A.

PROCEDURE 10

3-Nitrophthalates

A. From Alcohols Boiling below 150°. A mixture of 0.4 g. of 3-nitrophthalic anhydride and 0.5 ml. of the alcohol is refluxed gently in a test tube fitted with a glass tube for a condenser. The heating is continued for 5 to 10 minutes after the mixture liquefies. The mixture is cooled, diluted with 5 ml. of water, and heated to boiling. If solution is not complete, an additional 5 to 10 ml. of hot water is added. The solution is cooled and the ester allowed to crystallize. Sometimes the derivative separates as an oil and must be allowed to stand overnight to crystallize. The product is recrystallized once or twice from hot water.

B. From Alcohols Boiling above 150°. A mixture of 0.4 g. of 3-nitrophthalic anhydride, 0.5 g. of the alcohol, and 5 ml. of dry toluene is refluxed until all the anhydride has dissolved and then for 15 minutes more. The toluene is then removed by suction, using a water pump. The residue is extracted twice with 5 ml. of hot water, the residual oil is dissolved in 10 ml. of 95% alcohol, and the solution is heated to boiling. If the hot solution is not clear it should be filtered. Water is added to the hot solution until a turbidity is produced which is cleared up by the addition of a drop or two of alcohol. The solution is allowed to cool slowly and finally permitted to stand. Many of the higher alkyl 3-nitrophthalates derived from the monoalkyl ethers of ethylene glycol and diethylene glycol separate as oils and must be allowed to stand several days to solidify. Occasionally toluene may be substituted for the alcohol-water mixture for recrystallization. It is sometimes desirable to determine the neutralization equivalent of the alkyl acid phthalate as well as the melting point.

PROCEDURE 11

Benzylthiuronium Alkyl Hydrogen Sulfates

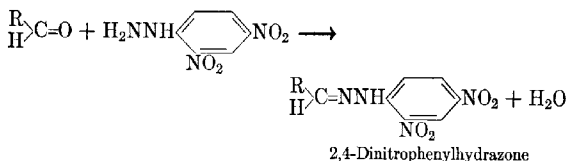
About 5 drops of the alcohol is added to a mixture of 4 drops of chlorosulfonic acid and 5 drops of dioxane. If hydrogen chloride is not immediately evolved, the resulting mixture is warmed gently with shaking

and allowed to stand for 5 or 10 minutes. Then, after the addition of 1 ml. of water, 1 ml. of a saturated aqueous solution (or 15% alcohol solution) of *S*-benzylthiuronium chloride is added. If crystals do not form in a few minutes the solution is chilled in an ice bath. The derivatives of the lower-molecular-weight alcohols (to *n*-hexyl inclusive) can be recrystallized from 10% ethanol, and derivatives of higher alcohols from 50% ethanol.

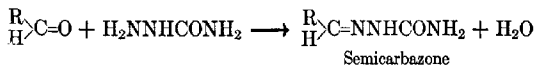
ALDEHYDES

(Listed on p. 229)

The most useful derivatives of aldehydes are the phenyl-, *p*-bromophenyl-, *p*-nitrophenyl-, and 2,4-dinitrophenylhydrazones (Procedures 14, 15). If, in the classification test with phenylhydrazine (Experiment 23, p. 116), a solid phenylhydrazone is obtained, it will, of course, be used as a derivative. However, if the phenylhydrazone is liquid, recourse must be had to one of the substituted phenylhydrazones; of these the 2,4-dinitrophenylhydrazones are to be recommended because they are all solids (Procedure 15).

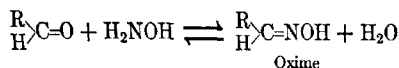


For low-molecular-weight, water-soluble aldehydes it is often advantageous to employ semicarbazide (Procedures 13A or 13B) as the reagent. All the semicarbazones are solids and generally can be obtained nearly pure without recrystallization. Sometimes these derivatives form slowly, and care must be taken to allow sufficient time for the reaction to go to completion.



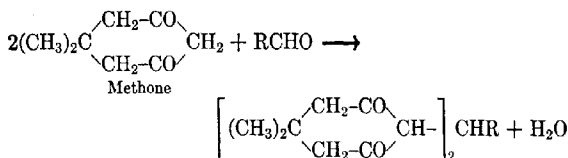
Oximes (Procedure 42) are often used, but in general these derivatives are likely to melt lower than the corresponding 2,4-dinitrophenylhydrazones and semicarbazones. An advantage of the oximes as derivatives is that they generally form rapidly.

The reaction between carbonyl compounds and hydroxylamine is reversible, and care must be taken to avoid unnecessary contact with strongly acid solutions; under these conditions the oxime may be reconverted to the original compound.



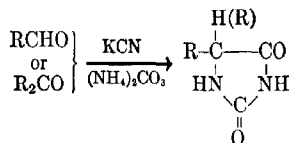
Aldehydes of high molecular weight are often conveniently identified by reference to the corresponding acids, which form when the aldehyde is oxidized (Procedures 12A and 12B).

Other derivatives which have been recommended for carbonyl compounds are phenylsemicarbazones, α - and β -naphthylhydrazones, *o*-, *m*-, and *p*-tolylsemicarbazones, α - and β -naphthylsemicarbazones, *p*-xenylsemicarbazones, 3,5-dinitrophenylsemicarbazones, *o*- and *p*-chlorobenzohydrazones, 3-nitrobenzohydrazones, nitroguanylhya zones, diphenylhydrazones, benzothiazoles, benzothiazolines, and the condensation products with methone (dimedon) (Procedure 16).



The last-named reagent is specific for aldehydes since ketones do not condense.

Both aldehydes and ketones react readily with ammonium carbonate and potassium (or sodium) cyanide to produce substituted hydantoins. These are crystalline solids and serve as useful derivatives.



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PROCEDURE 12

Oxidation to an Acid

A. Permanganate Method. A saturated solution of potassium permanganate in water is added to a solution or suspension of 1 g. of the aldehyde in 10 to 20 ml. of water to which a few drops of 10% sodium hydroxide solution have been added. The mixture is shaken vigorously, and sufficient permanganate is added to impart a definite purple color. The mixture is acidified with dilute sulfuric acid, and sodium bisulfite solution is added until the permanganate and manganese dioxide have been converted to manganese sulfate. The acid is removed by filtration and recrystallized from a water-acetone mixture. If the acid does not separate it may be recovered by extraction with chloroform or ether.

B. Hydrogen Peroxide Method. In a 500-ml. flask are placed 20 ml. of 5% sodium hydroxide solution and 30 ml. of 3% hydrogen peroxide solution. The solution is warmed to 65–70°, and 1 g. of the aldehyde is added. The mixture is shaken and kept at 65° for 15 minutes. If the aldehyde has not dissolved, a few milliliters of ethanol may be added. An additional 10 ml. of hydrogen peroxide is added, and the mixture is warmed for 10 more minutes. The solution is made acid to Congo red, and the acid that separates is removed by filtration.

If the acid is water soluble it is best to make the solution neutral to phenolphthalein and evaporate to dryness. The sodium salt of the acid is then converted to a suitable derivative by Procedure 1, 2, or 3.

PROCEDURE 13

Semicarbazones

A. For Water-soluble Compounds. One milliliter of the aldehyde or ketone, 1 g. of semicarbazide hydrochloride, and 1.5 g. of sodium acetate are dissolved in 10 ml. of water in a test tube. The mixture is vigorously shaken, and the test tube is placed in a beaker of boiling water and allowed to cool. It is then placed in a beaker of ice, and the sides of the tube are scratched with a glass rod. The crystals of the semicarbazone are removed by filtration and recrystallized from water or 25 to 50% ethanol.

B. For Water-insoluble Compounds. One milliliter of the aldehyde or ketone is dissolved in 10 ml. of ethanol. Water is added until the solu-

tion is faintly turbid, and the turbidity is removed with a few drops of ethanol. Then 1 g. of semicarbazide hydrochloride and 1.5 g. of sodium acetate are added, and from this point Procedure A is followed.

PROCEDURE 14

p-Nitrophenylhydrazones

A mixture of 0.5 g. of *p*-nitrophenylhydrazine, 0.5 g. of the aldehyde or ketone, and 10 to 15 ml. of ethanol is heated to boiling, and a drop of glacial acetic acid is added. The mixture is kept hot for a few minutes, and more ethanol is added if necessary to obtain a clear solution. The solution is cooled, and the *p*-nitrophenylhydrazone is collected on a filter. It may be recrystallized from a small amount of ethanol.

If the derivative does not separate from the solution on cooling, the mixture is heated to the boiling point, water is added until the solution is cloudy, and then a drop or two of ethanol is added to clarify it. The hydrazone that separates on cooling is recrystallized from a water-ethanol mixture.

PROCEDURE 15

2,4-Dinitrophenylhydrazones

A solution of 2,4-dinitrophenylhydrazine is prepared in the following fashion. To 0.4 g. of 2,4-dinitrophenylhydrazine in a 25-ml. Erlenmeyer flask is added 2 ml. of concentrated sulfuric acid. Water (3 ml.) is added dropwise, with swirling or stirring until solution is complete. To this warm solution is added 10 ml. of 95% ethanol.

A solution of the carbonyl compound in ethanol is prepared by dissolving 0.5 g. of the compound in 20 ml. of 95% ethanol. The freshly prepared 2,4-dinitrophenylhydrazine solution is added, and the resulting mixture is allowed to stand at room temperature. Crystallization of the 2,4-dinitrophenylhydrazone usually occurs within 5 to 10 minutes. If no precipitate is formed, the mixture is allowed to stand overnight.

Recrystallization can usually be effected in the following way. The 2,4-dinitrophenylhydrazone is heated on a steam cone with 30 ml. of ethanol (95%). If solution occurs immediately, water is added slowly until the cloud point is reached or until a maximum of 5 ml. of water has been added. If the dinitrophenylhydrazone does not dissolve, ethyl acetate is added slowly to the hot mixture until solution is attained. The hot solution is filtered through a fluted filter and allowed to stand at room temperature until crystallization is complete (about 12 hours).

PROCEDURE 16

Methone Derivatives of Aldehydes

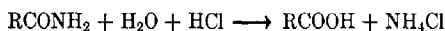
A. Aldehyde bis-Methone Condensation Products. To a solution of 0.1 g. of the aldehyde in 4 ml. of 50% ethanol is added 0.4 g. of methone, if the aldehyde is aliphatic. If an aromatic aldehyde is a possibility only, 0.3 g. of methone is used. One drop of piperidine is added, and the mixture is gently refluxed for 5 minutes. If the hot solution is clear at the end of this time, water is added dropwise to the cloud point. The mixture is then chilled, and the derivative, after being separated by filtration, is washed with 2 ml. of cold 50% ethanol. The derivative is recrystallized from mixtures of methanol and water.

B. Cyclization to Substituted Octahydroxanthenes. In the event that it is desirable to prepare an additional derivative, the above methone condensation product may be converted to a substituted octahydroxanthene by boiling a solution of 0.1 g. of the methone derivative in 80% ethanol (3 to 6 ml.) to which 1 drop of concentrated hydrochloric acid has been added. The cyclization is complete in 5 minutes, after which time water is added to the cloud point. The mixture is cooled and the substituted xanthene removed by filtration. This product is usually pure but it may be recrystallized from aqueous methanol.

AMIDES AND IMIDES

(Listed on p. 231)

The most general method for characterizing amides consists in hydrolyzing them with acids or alkalis (Experiment 28d, p. 136).

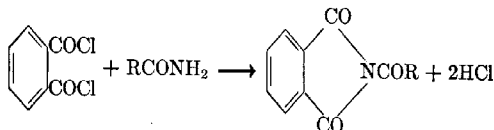


Hydrolysis of substituted amides yields primary or secondary amines instead of ammonia.

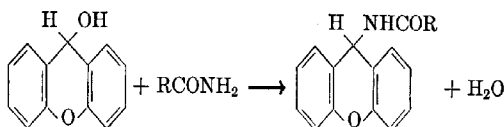


The identification is made by characterizing the products, viz., the acid, ammonia, and primary or secondary amine. The melting points of some of these hydrolysis products and their derivatives are given in Tables XIX and XXIII.

Phthalyl chloride reacts with unsubstituted amides to produce *N*-acylphthalimides which are useful solid derivatives.

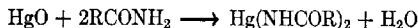


Xanthhyrol reacts readily with unsubstituted amides and imides to form 9-acylamidoxanthenes which are good derivatives (Procedure 17).



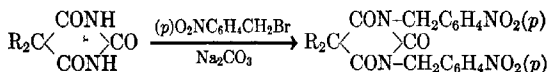
N-Substituted amides do not condense.

Mercuric oxide reacts with certain amides to form *N,N'*-mercuribisacylamides, which are high-melting solid derivatives.



A few amides form stable salts with oxalic acid, which serve for identification.

Barbiturates may be converted to *N,N'*-*p*-nitrobenzyl derivatives by reaction with *p*-nitrobenzyl bromide by a procedure similar to that for the preparation of *p*-nitrobenzyl esters of acids (Procedure 1).



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N,N'-Mercuribisacylamides. Williams, Rainey, and Leopold, *J. Am. Chem. Soc.*, **64**, 1738 (1942).
N,N'-*p*-Nitrobenzyl Barbiturates. Castle and Poe, *J. Am. Chem. Soc.*, **66**, 1440 (1944).

PROCEDURE 17

9-Acylamidoxanthenes

About 0.5 g. of xanthydroxol is dissolved in 7 ml. of glacial acetic acid. If the solution is not clear (owing to disproportionation products of xanthydroxol) it is allowed to stand a few minutes or centrifuged and the clear solution decanted into a clean test tube. To this solution is added 0.5 g. of the amide, and the mixture is warmed at 85° in a beaker of water for 20-30 minutes. Upon cooling, the acylamidoxanthene is collected on a filter and recrystallized from a mixture of 2 parts of dioxane and 1 of water.

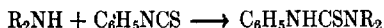
Some amides fail to dissolve in the acetic acid and may be converted to the derivative by using a mixture of 5 ml. of ethanol, 2 ml. of glacial acetic acid, and 3 ml. of water as the solvent for the reaction.

AMINES—PRIMARY AND SECONDARY

(Listed on p. 234)

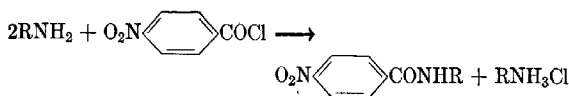
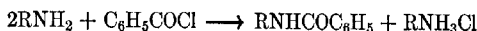
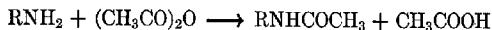
The most useful types of derivatives of primary and secondary amines are the corresponding acetamides and benzamides, phenylthioureas, and phenyl- and *p*-tolylsulfonamides. Of these the benzenesulfonamides are probably the most frequently used because the preparation of these derivatives is involved in the Hinsberg method for classifying amines (Experiment 4, p. 91; Procedure 19A). When the benzenesulfonamides prove unsuitable, recourse may be had to numerous similar derivatives each of which presents advantages in the identification of certain types of amines. *p*-Toluene- (Procedure 19A), *p*-bromobenzene- (Procedure 19B), *m*-nitrobenzene- (Procedure 14B), methane- (Procedure 19B), and α -naphthylsulfonamides (Procedure 19B) are recommended.

The phenylthioureas are especially valuable for characterizing low-molecular-weight, water-soluble amines. They are formed by reaction with phenyl isothiocyanate (Procedure 20).



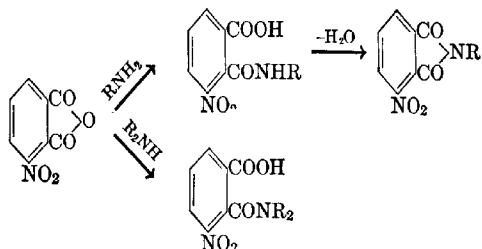
The reagent, phenyl isothiocyanate, is not sensitive to water; this reaction may be carried out with dilute aqueous solutions of the amines.

The amides of acetic (Procedure 18A), benzoic (Procedure 18B), and *p*-nitrobenzoic acids (Procedure 18C) are conveniently prepared by treatment of the amine, respectively, with acetic anhydride, benzoyl chloride, or *p*-nitrobenzoyl chloride.



Acetyl and benzoyl derivatives are known for nearly all primary and secondary amines, and for this reason these derivatives are very useful.

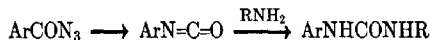
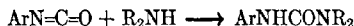
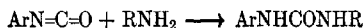
3-Nitrophthalic anhydride reacts with primary and secondary amines to produce phthalamic acids. The phthalamic acid from the primary amine undergoes dehydration when heated to 145° and forms the alkyl 3-nitrophthalimide. That from the secondary amine is stable to heat.



This reagent therefore offers an additional means of distinguishing among primary, secondary, and tertiary amines and furnishes derivatives for the primary and secondary amines.

Other types of derivatives which have been found valuable in the characterization of amines are 2,4-dinitrobenzal derivatives, azo compounds (Experiment 21, p. 113), salts of *p*-toluenesulfonic acid, molecular compounds with phenol, compounds with *p*-nitrobenzyl halides, and picrates (Procedure 23).

Primary and secondary amines combine with aryl isocyanates or acid azides to produce substituted ureas.



Phenyl-, α - and β -naphthyl-, *m*- and *p*-bromophenyl-, *m*- and *p*-chlorophenyl-, *m*- and *p*-nitrophenyl-, and 3,5-dinitrophenylureas have been described.

A number of amine hydrochlorides may be obtained by passing dry hydrogen chloride into an ether or benzene solution of the amine. Some of the hydrochlorides have satisfactory melting or decomposition points and hence may serve as derivatives.

Hydrochlorides of amino alcohols are best made by neutralizing *n*-propyl alcohol solutions of the alkanolamines with dry hydrogen chloride.

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PROCEDURE 18

Amides from Amines

A. Substituted Acetamides from Class B Amines. A solution of the amine is prepared by dissolving about 0.5 g. of the compound in 50 ml. of 5% hydrochloric acid. Small portions of a 5% sodium hydroxide solution are added until the mixture becomes cloudy; the turbidity is then removed by adding 2–5 ml. of 5% hydrochloric acid. A few chips of ice are added, followed by 5 ml. of acetic anhydride. The mixture is stirred or swirled vigorously, and a previously prepared solution of 5 g. of sodium acetate (trihydrate) in 50 ml. of water is added in one portion. If the product does not crystallize, the mixture is chilled overnight.

Recrystallization may be effected from cyclohexane or from a mixture of cyclohexane and benzene. The acetamide must be thoroughly dry before recrystallization is attempted from these solvents. An ethanol-water mixture may also be used for recrystallization.

B. Substituted Benzamides. Pyridine Method. To a solution of 0.5 g. of the compound in 5 ml. of dry pyridine and 10 ml. of dry benzene is added, dropwise, 0.50 ml. of benzoyl chloride. The resulting mixture

is heated in a water bath at 60–70° for 30 minutes and is then poured into 100 ml. of water. The benzene layer is separated, and the aqueous solution is washed once with 10 ml. of benzene. The combined benzene solutions are washed with water and with 5% sodium carbonate solution and dried with a little anhydrous magnesium sulfate. The drying agent is removed by filtration through a fluted filter, and the benzene is evaporated to a small volume (3–4 ml.). Hexane (about 20 ml.) is stirred into the mixture, and the crystalline benzoyl derivative is removed by filtration and washed with hexane. Recrystallization may usually be effected from a mixture of cyclohexane and hexane or from a mixture of cyclohexane and ethyl acetate. Ethanol or aqueous ethanol may also be used with many compounds.

C. Substituted Benz- and *p*-Nitrobenzamides. The regular procedure for the Schotten-Baumann reaction described under Experiment 1e, page 88, may be used. Two modified procedures are the following:

(a) A mixture of 20 ml. of 5% sodium hydroxide solution, 5 ml. of chloroform, 0.5 g. of the compound, and 0.5 ml. of benzoyl chloride is shaken or stirred for about 20 minutes and then allowed to stand for 12 hours. The chloroform layer is separated, and the aqueous layer is washed with 10 ml. of chloroform. The combined chloroform solutions are washed with water, dried with anhydrous magnesium sulfate, and evaporated to a small volume (2–3 ml.). Hexane (20–25 ml.) is stirred into the solution, and the derivative is removed by filtration and washed with hexane.

(b) About 1 ml. of the amine is added to a solution of 1 g. of benzoyl chloride or *p*-nitrobenzoyl chloride in 20 ml. of dry benzene. The resulting solution is boiled for 15 minutes under a reflux condenser and is then allowed to cool. The solution is filtered, and the precipitate is washed with 10 ml. of warm benzene, the washings being added to the original filtrate. The benzene solution is next washed with 10 ml. of 2% sodium carbonate solution, then with 10 ml. of 2% hydrochloric acid, and finally with 10 ml. of distilled water. The benzene is evaporated, and the residue is recrystallized from dilute ethanol.

PROCEDURE 19

Sulfonamides from Amines

A. Benzene- and *p*-Toluenesulfonamides. These derivatives are prepared by the procedure outlined in Experiment 4, page 91, sufficient amounts of material being used to permit recrystallization of the final product from 95% ethanol.

B. Benzyl-, *p*-Bromobenzene-, *m*-Nitrobenzene-, α -Naphthyl-, and Methanesulfonamides. A solution of 1 g. of the sulfonyl chloride in

25 ml. of dry benzene is prepared, and 2 ml. of the amine is added. The solution is shaken and allowed to stand for 10 minutes. The amine hydrochloride is removed by filtration, and the filtrate is evaporated. The residue is recrystallized once or twice from dilute ethanol.

PROCEDURE 20

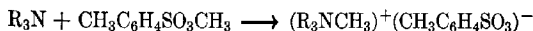
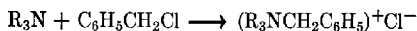
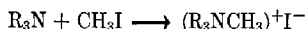
Phenylthioureas

Equal amounts of the amine and phenyl isothiocyanate are mixed in a test tube and shaken for 2 minutes. If no reaction occurs spontaneously the mixture is heated for 3 minutes over a low flame. The aliphatic amines usually react immediately whereas the aromatic amines require heating. The mixture is then kept in a beaker of ice until the mass solidifies. The solid is powdered and washed with ligroin and 50% ethanol in order to remove any excess of either reactant. The residue is then recrystallized from 95% ethanol.

AMINES—TERTIARY

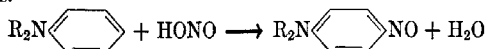
(Listed on p. 242)

Tertiary amines vary so greatly in nature that no type of derivative has been found to be generally applicable. Perhaps the most useful derivatives are the quaternary ammonium salts formed by the combination of the amine with methyl iodide (Procedure 21A), benzyl chloride (Procedure 21B), or methyl *p*-toluenesulfonate (Procedure 21B).



The salts of halogen acids, picric acid (Procedure 23), *p*-toluenesulfonic acid, and chloroplatinic acid are also employed frequently.

Certain *N,N*-dialkylanilines react with nitrous acid to give *p*-nitroso derivatives, and these may sometimes serve as derivatives.



REFERENCE

Marvel, Scott, and Amstutz, *J. Am. Chem. Soc.*, **51**, 3638 (1929).

PROCEDURE 21

Quaternary Ammonium Salts of Tertiary Amines

A. A mixture of 0.5 g. of the amine and 0.5 ml. of methyl iodide is warmed in a test tube over a low flame for a few minutes and is then cooled in an ice bath. The tube is scratched with a glass rod to hasten crystallization. The product is purified by recrystallization from absolute ethyl or methyl alcohol or from ethyl acetate.

B. One gram of the amine is added to a solution of 2 to 3 g. of benzyl chloride or methyl *p*-toluenesulfonate in 10 ml. of dry benzene. The solution is boiled for 10 to 20 minutes and cooled. The products are recrystallized by dissolving them in the least possible amount of boiling ethanol; ethyl acetate is added until precipitation starts, and the mixture is cooled. The product is removed by filtration and quickly dried by being rubbed on a clay plate; the melting point is determined immediately.

PROCEDURE 22

Nitroso Compounds

Two grams of the amine is dissolved in 20 ml. of 10% hydrochloric acid, and the solution is cooled in a freezing mixture. A solution of 1.5 g. of sodium nitrite dissolved in 2 ml. of water is added slowly with vigorous stirring. The mixture is allowed to stand 15 minutes in the ice bath, and then the hydrochloride of the nitroso compound is collected on a filter. The yellow crystals are mixed with 3 ml. of water and placed in an ice bath. Dilute sodium hydroxide solution is added until the solution is alkaline. The green nitroso compound is extracted with ether, and the ether is allowed to evaporate. The nitroso compound is deposited as brilliant green crystals. These are collected on a filter and dried on a porous plate.

PROCEDURE 23

Picrates

A. A sample of the compound (0.3 to 0.5 g.) is added to 10 ml. of 95% ethanol. If solution is not complete the mixture is shaken until a saturated solution results and is then filtered. The filtrate is added to 10 ml. of a saturated solution of picric acid in 95% ethanol, and the solution is heated to boiling. The solution is allowed to cool slowly, and the yellow crystals of the picrate are removed by filtration and recrystallized from ethanol. Certain picrates, especially those of hydrocarbons (Table

XXXIV), dissociate when heated and consequently cannot be recrystallized. In such cases the original precipitate should be washed with a very small amount of ether and dried on a clay plate in preparation for the melting-point determination. (Caution: Some picrates explode when heated.)

B. Equal amounts of the compound and picric acid are mixed in a test tube, which is then heated on the steam cone for 10 minutes or over a very low flame until the mixture melts. The solid is allowed to cool and, if sufficiently stable, is recrystallized from ethanol.

AMINO ACIDS

(Listed on p. 245)

The melting points or decomposition points of amino acids are not exact. The values depend on the rate of heating. Hence, in using these constants to prepare a list of possibilities, allowance must be made for their inaccuracy. Use must also be made of the many specific tests and color reactions which have been developed for the amino acids.

Solid derivatives of the amino acids are usually obtained by reference to derivatives of the type used for amines rather than those described for acids. The Schotten-Baumann reaction (Experiment 1e, p. 88) yields the benzoyl derivative, and the same general procedure using acetic anhydride in place of benzoyl chloride leads to the acetyl derivatives (Procedure 18A). Phenyl isocyanate reacts with amino acids to produce the corresponding substituted phenylureas (Procedure 6A). The Hinsberg reaction, using *p*-toluenesulfonyl chloride (Procedure 24), furnishes good derivatives for a considerable number of the amino acids.

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p-Toluenesulfonyl Derivatives of Amino Acids. McChesney and Swann, *J. Am. Chem. Soc.*, **59**, 1116 (1937).

3,5-Dinitrobenzoyl Derivatives of Amino Acids. Saunders, *Biochem. J.*, **28**, 580 (1934); Town, *ibid.*, **35**, 578 (1941).

PROCEDURE 24

p-Toluenesulfonyl Derivatives of Amino Acids

About 1 g. of the amino acid is dissolved in 20 ml. of 1 *N* sodium hydroxide solution, an ethereal solution of 2 g. of *p*-toluenesulfonyl chloride in 25 ml. of ether is added, and the mixture shaken mechanically or vigorously stirred for 3 to 4 hours. The ether layer is separated, and the aqueous layer is acidified to Congo red with dilute hydrochloric acid. The derivative usually separates as a solid which is removed by filtration and recrystallized from 4 to 5 ml. of 60% ethanol. If an oil is obtained upon acidification, the mixture is placed in a refrigerator overnight to induce crystallization.

The sodium salts of the derivatives of phenylalanine and tyrosine are sparingly soluble in water and separate during the initial reaction. The resulting suspension is acidified, and the salts go into solution. The *p*-toluenesulfonyl derivatives then crystallize from the ether layer and are removed by filtration.

The derivatives of glutamic and aspartic acids, arginine, lysine, tryptophane, and proline crystallize with difficulty; other derivatives should be tried in the event that oils are produced.

CARBOHYDRATES AND GLYCOSIDES

(Listed on p. 247)

The osazones (Experiment 23b, p. 116) give useful information concerning the common sugars. The crystalline form of the osazone should be compared under the microscope with that of an authentic specimen. According to Mulliken, the relative rates of formation of the osazones are significant. The melting points of individual osazones often lie too close together to serve as a means of identification.

Other derivatives which are valuable in the identification of carbohydrates are acetates (Procedures 8A or 8B), benzoates (Procedure 7A), acetone derivatives, and benzaldehyde derivatives.

Characteristic derivatives of the aldoses may be obtained by formation of the acetylated diethyl mercaptals.

A systematic series of tests has been worked out by Dehn, Jackson, and Ballard, whose article should be consulted.

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 Armstrong and Armstrong, *The Carbohydrates*, Longmans, Green, and Co., New York, 1934.
Mercaptal Acetates of the Aldoses. Wolfson and Karabinos, *J. Am. Chem. Soc.*, **67**, 500 (1945).

ESTERS

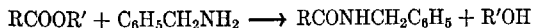
(Listed on p. 248)

Saponification equivalents (pp. 133 and 134) and specific gravities will be found to be very helpful in addition to the boiling point in preparing a list of possible compounds.

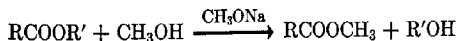
Because of difficulties involved in the separation and purification of the hydrolysis products, it is best to prepare derivatives by reactions on the original ester. Esters containing other functional groups may often be identified by reference to solid derivatives obtained by reactions such as halogenation, nitration, and acylation.

Derivatives of the acyl part of the ester may be obtained by the following methods.

1. Reaction with benzylamine in the presence of a little ammonium chloride yields *N*-benzylamides, which serve as derivatives (Procedure 25).

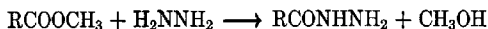


The reaction proceeds well when R' is methyl or ethyl. Esters of higher alcohols should be subjected to a preliminary methanolysis.



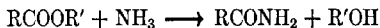
The methyl ester, thus obtained, may be used for the aminolysis.

2. Hydrazine reacts readily with methyl and ethyl esters to produce acid hydrazides, which serve as satisfactory derivatives (Procedure 26).



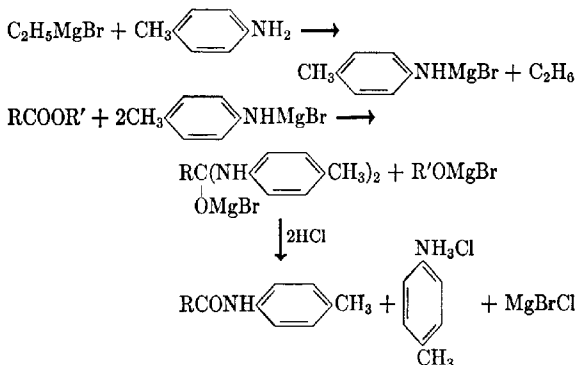
Esters of the higher alcohols should be converted to the methyl esters.

3. Some simple esters react with aqueous or alcoholic ammonia to produce amides which serve as derivatives.

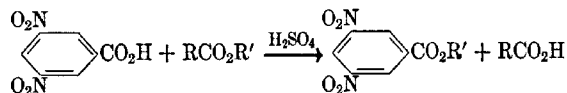


However, most esters must be heated under pressure in order to effect this reaction.

4. The *p*-toluide of the acidic portion of the ester may be obtained by means of the following reactions.



Conversely, a solid derivative of the alcohol portion of a simple ester may be obtained by effecting an interchange reaction between 3,5-dinitrobenzoic acid and the ester in the presence of concentrated sulfuric acid (Procedure 27).



The method is applicable to a large number of simple esters but may not be used if either the R or R' group of the ester reacts

with concentrated sulfuric acid. High-molecular-weight esters (> 250) also fail to react.

If it is not possible to obtain derivatives of the acid and alcohol portions directly from the ester, recourse must be had to hydrolysis, which is best accomplished by saponification with alkali according to Experiment 28 (p. 128). The exact procedure to be followed in working up the saponification mixture depends on the nature of the acid and hydroxy compound. The acid may be monobasic or polybasic and soluble or insoluble in water. The hydroxy compound may be a monatomic alcohol, a polyatomic alcohol, or a phenol. Hence the separation and characterization of the products of saponification must be planned carefully in the light of the suggestions obtained from the list of possibilities and the results from classification reactions.

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Acid Hydrazides from Esters. Sah, *Rec. trav. chim.*, **59**, 1036 (1940).
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PROCEDURE 25

N-Benzylamides from Esters

A mixture of 1 g. of the ester, 3 ml. of benzylamine, and 0.1 g. of powdered ammonium chloride is refluxed for 1 hour in a Pyrex test tube fitted with a small finger condenser. After being cooled, the reaction mixture is washed with water to remove excess benzylamine and to induce crystallization. Often the addition of a little dilute hydrochloric acid will promote crystallization. An excess of acid must be avoided since it dissolves N-benzylamides. Occasionally the presence of unchanged ester may prevent crystallization. In that case it is best to boil the solution a few minutes with water in an evaporating dish to volatilize the ester. The solid amide is collected on a filter, washed with a little ligroin, and recrystallized from a mixture of ethanol and water or of acetone and water.

Esters of alcohols higher than ethanol should be refluxed for 30 minutes with 5 ml. of absolute methanol in which a small piece of sodium (0.1 g.)

has been dissolved. At the end of the reflux period, the methanol is evaporated and the residue treated by the above procedure.

PROCEDURE 26

Acid Hydrazides from Esters

One gram of the methyl or ethyl ester and 1 ml. of 85% hydrazine hydrate are mixed, and the mixture is heated under reflux for 15 minutes. Just enough absolute ethanol is then added, through the top of the condenser, to obtain a clear solution. After the mixture has been heated under reflux for 2 hours, the alcohol is evaporated and the residue cooled. The crystals of the hydrazide are collected on a filter and recrystallized from water or a mixture of water and ethanol.

Higher esters must be subjected to methanolysis, as described above, before treatment with hydrazine.

PROCEDURE 27

Alkyl 3,5-Dinitrobenzoates from Esters

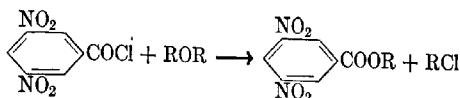
About 2 ml. of the ester is mixed with 1.5 g. of 3,5-dinitrobenzoic acid, and 2 drops of concentrated sulfuric acid is added. If the original ester boiled below 150°, the mixture is heated gently under reflux. If the ester boiled above 150°, the mixture is heated in an oil bath at 150°, with frequent stirring. The time required varies from 30 minutes to 1 hour, the longer time being used in those cases in which the 3,5-dinitrobenzoic acid fails to dissolve in about 15 minutes. After the mixture has been cooled, 25 ml. of absolute ether is added, and the solution is extracted twice with two portions of 15 ml. of 5% sodium carbonate solution to remove the sulfuric and 3,5-dinitrobenzoic acids. The ether layer is washed with 10 ml. of water, and the solvent is evaporated. The residue (usually an oil) is dissolved in 5 ml. of boiling ethanol. After the solution has been filtered, water is added to incipient cloudiness. The mixture is cooled and stirred to induce crystallization of the derivative.

ETHERS—ALIPHATIC

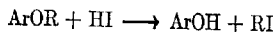
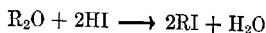
(Listed on p. 252)

The only method suitable for the preparation of solid derivatives for the identification of small amounts of aliphatic ethers involves the cleavage of the ethers and the formation of the corre-

sponding 3,5-dinitrobenzoates. This is accomplished by treating the ether with 3,5-dinitrobenzoyl chloride in the presence of zinc chloride (Procedure 28).

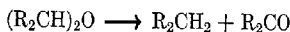
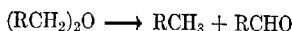


This method is not suitable for mixed ethers in which both the radicals of the ether are aliphatic. Aliphatic ethers and aryl alkyl ethers may be cleaved by hydriodic acid (Experiment 14).



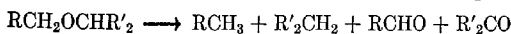
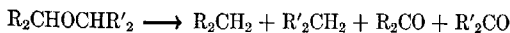
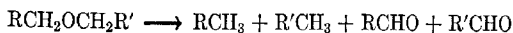
By use of a large sample (5 to 10 g.), the alkyl iodide may be isolated and converted to a derivative (Procedures 33, 34, 35, 36). The phenol from an aryl alkyl ether may be isolated also and transformed into a derivative (Procedures 46, 47, 48).

Since pyrolysis of ethers at 500° produces chiefly hydrocarbons and carbonyl compounds, this reaction may be used for their characterization.



The vapors from the pyrolysis are condensed and treated with suitable reagents, such as *o*-tolylsemicarbazide, *p*-tolylsemicarbazide, *m*-nitrobenzhydrazide, and *p*-chlorobenzhydrazide, to produce substituted semicarbazones which serve as derivatives.

Unsymmetrical ethers produce a mixture of aldehydes or ketones, and these must be separated by fractionation in order to obtain pure derivatives.



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- Alkyl 3,5-Dinitrobenzoates from Ethers.** Underwood, Baril, and Toone, *J. Am. Chem. Soc.*, **52**, 4087 (1930).
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PROCEDURE 28

Alkyl 3,5-Dinitrobenzoates from Ethers

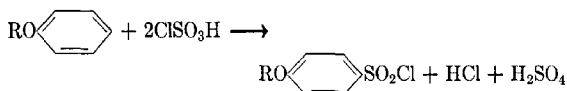
A mixture of 1 ml. of the ether, 0.15 g. of anhydrous zinc chloride, and 0.5 g. of 3,5-dinitrobenzoyl chloride is placed in a test tube which is then attached to a reflux condenser. The mixture is refluxed for 1 hour and cooled. To it is then added 10 ml. of sodium carbonate solution. The mixture is warmed to 90° in a water bath, cooled, and filtered. The precipitate is washed with 5 ml. of 5% sodium carbonate solution and 10 ml. of distilled water. The residue is dissolved in 10 ml. of hot carbon tetrachloride, and the solution is filtered while hot; the filtrate is then cooled in an ice bath. If the ester does not separate, the carbon tetrachloride is evaporated. The residue is dried on a porous plate, and the melting point is determined.

ETHERS—AROMATIC

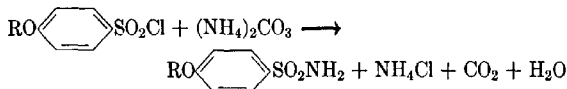
(Listed on p. 253)

The derivatives of aromatic ethers which are employed most frequently are those obtained by bromination (Procedure 29) and nitration (Procedures 39A and 39B). Picrates (Procedure 32) are also used.

Aromatic ethers react smoothly with chlorosulfonic acid at 0° to produce sulfonyl chlorides (Procedure 30).



The latter are oils or low-melting solids and are treated with ammonia or ammonium carbonate (Procedure 31). The sulfonamides obtained in this way are useful derivatives.

**REFERENCES**

- Picrates.** Baril and Megrdichian, *J. Am. Chem. Soc.*, **58**, 1415 (1936).
Picrates of Alkyl Naphthyl Ethers. Dermer and Dermer, *J. Org. Chem.*, **3**, 289 (1938).

Sulfonamides of Aryl Ethers. Huntress and Carten, *J. Am. Chem. Soc.*, **62**, 603 (1940).

PROCEDURE 29

Bromination

One gram of the compound is dissolved in 15 ml. of glacial acetic acid, and 3 to 5 g. of liquid bromine is added. The mixture is allowed to stand for 15 to 30 minutes and is then poured into 50 to 100 ml. of water. The bromo compound which separates is removed by filtration and purified by recrystallization from dilute ethanol. In some cases carbon tetrachloride may be substituted for the acetic acid as the solvent: the carbon tetrachloride is distilled, and the residue is recrystallized.

PROCEDURE 30

Sulfonyl Chlorides

A solution of 1 g. of the compound in 5 ml. of dry chloroform in a clean, dry test tube is cooled in a beaker of ice to 0°. About 5 g. of chlorosulfonic acid is added dropwise, and after the initial evolution of hydrogen chloride has subsided the tube is removed from the ice bath and allowed to warm up to room temperature (about 20 minutes). The contents of the tube are poured into a 50-ml. beaker full of cracked ice. The chloroform layer is removed and washed with water. The chloroform is evaporated, and the residual sulfonyl chloride is recrystallized from low-boiling petroleum ether, benzene, or chloroform.

PROCEDURE 31

Sulfonamides

The sulfonyl chloride (0.5 g.) is mixed with 2.0 g. of dry powdered ammonium carbonate and heated at 100° for 30 minutes. The mixture is cooled and washed with three 10-ml. portions of cold water. The crude sulfonamide is dissolved in 10 ml. of 5% sodium hydroxide solution, gentle heating being used if necessary, and the solution is filtered to remove any sulfone or chlorinated products. The filtrate is acidified with dilute hydrochloric acid, and the sulfonamide is removed by filtration. It is purified by recrystallization from dilute ethanol and dried at 100°.

PROCEDURE 32

Picrates of Phenolic Ethers

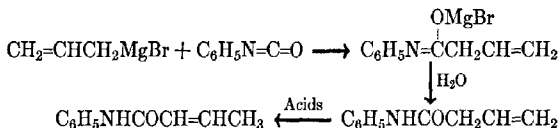
A solution of 1 to 2 g. of the ether in the smallest possible amount of chloroform (2 to 10 ml.) is added to a separately prepared solution of 2 g. of picric acid in 10 ml. of boiling chloroform. The mixture is stirred thoroughly, set aside, and allowed to cool. The picrate crystallizes when the mixture is allowed to stand. It may be purified by recrystallization from the smallest possible amount of boiling chloroform. The melting point should be determined as soon as possible since some picrates decompose.

HALIDES—ALKENYL

(Listed on p. 254)

Many of the unsaturated halogen compounds may be identified by reference to their physical constants.

In certain cases Grignard reagents may be obtained by means of special procedures and converted to anilides of unsaturated acids. Rearrangements sometimes occur. For example, allylmagnesium bromide and phenyl isocyanate yield an oil which rearranges in contact with acids to give crotonanilide.



REFERENCES

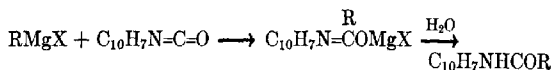
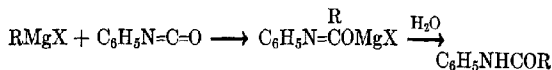
- Anilides. Schwartz and Johnson, *J. Am. Chem. Soc.*, **53**, 1063 (1931).
 Allylmagnesium Bromide. Gilman and McGlumphy, *Bull. soc. chim.*, (4), **43**, 1322 (1928).

HALIDES—ALKYL AND CYCLOALKYL

(Listed on p. 255)

The best methods for making derivatives of alkyl and cycloalkyl halides depend on their conversion into the corresponding Grignard reagents. The anilides, toluides, and α -naphthalides

prepared from the Grignard reagents (Procedure 34) by treatment with phenyl, *p*-tolyl, and α -naphthyl isocyanate, respectively, are the derivatives most frequently used.



If the halide is primary the Grignard reagent may be converted to the corresponding alkylmercuric halide by treatment with the proper mercuric halide (Procedure 33).



The mercury salt and the alkyl halide should be derived from the same halogen, for otherwise mixtures of alkylmercuric halides may be obtained. This method fails with tertiary alkyl halides.

Among the many other important derivatives of alkyl halides may be mentioned the 3,5-dinitrobenzoates, the *N*-alkylphthalimides, *N*-alkyl-3-nitrophthalimides, *N*-alkyltetrachlorophthalimides, alkyl β -naphthyl ethers (Procedure 35), *S*-alkylthiourea picrates (Procedure 35), *N*-alkylsaccharins, alkyl triiodophenyl ethers, *p*-alkoxybenzoic acids, *N*-alkyl-*p*-bromobenzenesulfon-*p*-anisides, and *N*-alkyl-*p*-toluenesulfonoluides.

Derivatives of alkyl and cycloalkyl halides are particularly useful not only because these compounds are encountered frequently but also because they are readily made from alcohols, and so furnish an indirect way of identifying the alcohols. All the preceding methods are to be used with caution in view of the fact that rearrangements sometimes occur.

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 α -Naphthalides. Gilman and Furry, *J. Am. Chem. Soc.*, **50**, 1214 (1928).
Anilides, Toluides, and α -Naphthalides. Underwood and Gale, *J. Am. Chem. Soc.*, **56**, 2117 (1934).

- Alkylmercuric Halides.** Marvel, Gauerke, and Hill, *J. Am. Chem. Soc.*, **47**, 3009 (1925); Slotta and Jacobi, *J. prakt. Chem.*, **120**, 249 (1929); Hill, *J. Am. Chem. Soc.*, **50**, 167 (1928).
- N-Alkyl-3-nitrophthalimides.** Sah and Ma, *Ber.*, **65**, 1630 (1932).
- N-Alkyltetrachlorophthalimides.** Allen and Nicholls, *J. Am. Chem. Soc.*, **56**, 1409 (1934).
- S-Alkylisothioureia Picrates.** Brown and Campbell, *J. Chem. Soc.*, **1937**, 1699.
- Alkylsaccharins.** Merritt, Levey, and Cutter, *J. Am. Chem. Soc.*, **61**, 15 (1939).
- Alkyl Triiodophenyl Ethers.** Drew and Sturtevant, *J. Am. Chem. Soc.*, **61**, 2666 (1939).
- p-Alkoxybenzoic Acids.** Lauer, Sanders, Leckley, and Ungnade, *J. Am. Chem. Soc.*, **61**, 3050 (1939).
- N-Alkyl-p-bromobenzene sulfon-p-anisides.** Gillespie, *J. Am. Chem. Soc.*, **56**, 2740 (1934).
- N-Alkyl p-Toluenesulfonoluides.** Young, *J. Am. Chem. Soc.*, **56**, 2167, 2783 (1934); **57**, 773 (1935).

PROCEDURE 33

Alkylmercuric Halides

The Grignard reagent is made from the alkyl halide by treating 0.3 g. of magnesium in 15 ml. of dry ether with 1 ml. of the alkyl halide in a clean, dry test tube. A crystal of iodine is added to start the reaction. When the reaction is complete the solution is filtered through a little glass wool and the filtrate allowed to flow into a test tube containing 4 to 5 g. of mercuric chloride, bromide, or iodide, depending on the halogen in the original alkyl halide. The reaction mixture is shaken vigorously, warmed on the steam cone for a few minutes, and evaporated to dryness. The residue is boiled with 20 ml. of 95% ethanol, and the solution is filtered. The filtrate is diluted with 10 ml. of water and cooled in an ice bath. The alkylmercuric halide which separates is collected on a filter and recrystallized from 60% ethanol.

PROCEDURE 34

Anilides, Toluides, and Naphthalides from Alkyl Halides

The Grignard reagent is prepared as in Procedure 33 and is treated with 0.5 ml. of phenyl, p-tolyl, or α -naphthyl isocyanate dissolved in 10 ml. of absolute ether. The mixture is shaken and allowed to stand 10 minutes. About 25 ml. of 2% hydrochloric acid is added, with very vigorous shaking. The ether layer is separated and dried with magnesium

sulfate, and the ether is distilled. The residue is recrystallized from methanol, ether, or petroleum ether.

PROCEDURE 35

Alkyl β -Naphthyl Ethers

To a solution of 0.6 g. of sodium hydroxide in 25 ml. of ethanol are added 2 g. of β -naphthol and 2 g. of the alkyl halide. If the halide is a chloride, 0.5 g. of potassium iodide is added also.¹ The mixture is heated under reflux for 30 minutes and poured into 75 ml. of cold water. This mixture is made distinctly alkaline to phenolphthalein and stirred vigorously. The alkyl β -naphthyl ether is removed by filtration and recrystallized from ethanol or an ethanol-water mixture.

PROCEDURE 36

S-Alkylisothiurea Picrates

A mixture of 0.5 g. of powdered thiourea, 0.5 g. of the alkyl bromide or iodide, and 5 ml. of 95% ethanol is placed in a test tube and boiled for 2 minutes. In another test tube 0.4 g. of picric acid is dissolved in the minimum amount of boiling ethanol. The two solutions are mixed and allowed to cool. The *S*-alkylisothiurea picrate is removed by filtration and recrystallized from ethanol.

Alkyl chlorides may sometimes be induced to react by adding 1 g. of potassium iodide to the original reaction mixture. Sufficient ethanol or water must be added to produce a clear solution at the boiling point. The subsequent procedure is the same as outlined above.

HALIDES—HALOGEN DERIVATIVES OF AROMATIC
HYDROCARBONS

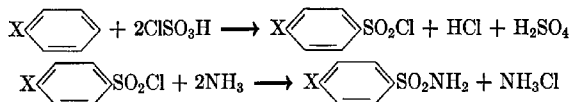
(Listed on p. 256)

Many excellent methods are available for making suitable derivatives of halogen derivatives of aromatic hydrocarbons. The most general of these is nitration (Procedure 39B). However, bromine and chlorine derivatives having one side chain are frequently oxidized to the corresponding acids (Procedures 40A

¹ This procedure is useful occasionally for making derivatives of dihalides of the type $X(CH_2)_nX$. Potassium iodide must not be added if the compound is a 1,2-dihalide ($n = 2$). Why?

and 40B). For aryl iodides and bromides conversion to the corresponding carboxylic acids or anilides (Procedure 34) is recommended.

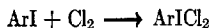
Aryl halides react readily with chlorosulfonic acid to produce sulfonyl chlorides (Procedure 37), which yield sulfonamides when treated with ammonia (Procedure 38).



Two abnormal reactions may take place during the sulfonation. Fluorobenzene, iodobenzene, *o*-dichlorobenzene, and *o*-dibromobenzene yield the corresponding sulfones when treated with chlorosulfonic acid at 50° in the absence of a solvent. These sulfones are solids and will serve as derivatives. In other cases small amounts of sulfones may be produced but are separable from the sulfonamide since they are insoluble in alkali. A second abnormal reaction is nuclear chlorination. This reaction takes place with *p*-diiodobenzene and 1,2,4,5-tetrachlorobenzene. Unsatisfactory results are obtained in the case of iodo derivatives of aromatic hydrocarbons.

Aryl halides, in which the halogen atom is activated by nitro groups, react readily with piperidine to form useful piperidyl derivatives.

Aryl iodides take up chlorine to form iodoaryl dichlorides which may serve as derivatives.



REFERENCES

- Arylsulfonamides.** Huntress and Carten, *J. Am. Chem. Soc.*, **62**, 511 (1940).
Piperidyl Derivatives of Aromatic Halogeno-nitro Compounds. Seikel, *J. Am. Chem. Soc.*, **62**, 750 (1940).
Iodoaryl Dichlorides. Nichol and Sandin, *J. Am. Chem. Soc.*, **67**, 1307 (1945).

PROCEDURE 37

Sulfonyl Chlorides

A solution of 1 g. of the compound in 5 ml. of dry chloroform in a clean, dry test tube is cooled in a beaker of ice to 0°. About 5 ml. of

chlorosulfonic acid is added dropwise, and after the initial evolution of hydrogen chloride has subsided the tube is removed from the ice bath and allowed to warm up to room temperature (about 20 minutes). The contents of the tube are poured into a 50-ml. beaker full of cracked ice. The chloroform layer is removed and washed with water, and the chloroform is evaporated. The residual crude sulfonyl chloride may be recrystallized from low-boiling petroleum ether, benzene, or chloroform.

Note. The above conditions are satisfactory for most of the simple aryl halides and for alkylbenzenes. For the halotoluenes it is desirable to warm the chloroform solution to 50° for 10 minutes and then pour the mixture on cracked ice. Polyhalogen derivatives require more drastic treatment. For such compounds the sulfonation is carried out without any solvent, and the sulfonation mixture is warmed to 100° for 1 hour under a reflux condenser.

PROCEDURE 38

Sulfonamides

About 0.5 g. of the sulfonyl chloride is boiled with 5 ml. of concentrated ammonium hydroxide for 10 minutes. The mixture is diluted with 10 ml. of water, cooled, and filtered.

The crude sulfonamide is dissolved in 10 ml. of 5% sodium hydroxide solution, with gentle heating, if necessary, and the solution is filtered to remove any sulfone or chlorinated products. The filtrate is acidified with dilute hydrochloric acid, and the sulfonamide is removed by filtration. It is purified by recrystallization from dilute ethanol and dried at 100°.

HALIDES—POLYHALOGEN DERIVATIVES OF NON-BENZENOID HYDROCARBONS

(Listed on p. 258)

General methods for preparing solid derivatives of polyhalogen derivatives of non-benzenoid hydrocarbons have not been developed, and, as a consequence, identification usually depends on physical properties. However, among members of a given series the variations in physical constants are in general greater than with the parent hydrocarbons and, as a result, constitute a more useful basis for identification.

Special methods for preparing derivatives of certain classes of polyhalogen derivatives of the type under consideration are, how-

ever, available in a number of instances. Thus, alkyl halides carrying haloaryl substituents may be treated as simple alkyl halides or as monoalkylbenzenes.

HYDROCARBONS—AROMATIC

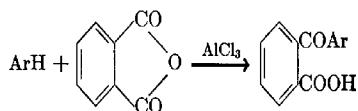
(Listed on p. 259)

The most useful derivatives of aromatic hydrocarbons are those obtained by nitration (Procedure 39). Highly alkylated benzenes have been identified by nitration followed by reduction of the nitro compounds to the amines, which are then acetylated or benzoylated to give mono- or diacetamino or benzamino derivatives.



Aromatic hydrocarbons which have side chains may be oxidized to the corresponding acids. If there is only one such chain this is usually an excellent method. Permanganate oxidation (Procedure 40B) is best for this purpose. Aromatic acids having several carboxyl groups are sometimes difficult to handle, and it is for this reason that the utility of the oxidation method is limited. If there are two side chains situated in adjacent positions on the ring, oxidation is recommended because the resulting acid (*o*-phthalic acid) is easy to identify. *o*-Dialkylbenzenes undergo fundamental decomposition with chromic acid (Procedure 40A). Since this oxidizing agent may give misleading results, the permanganate oxidation should always be used (Procedure 40B). The melting points of the acids obtained by oxidation of the alkylbenzenes may be obtained by reference to the table on page 223.

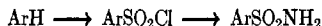
Aromatic hydrocarbons and their halogen derivatives undergo the Friedel-Crafts reaction with phthalic anhydride, producing arylbenzoic acids in good yield (Procedure 41).



Picric acid combines with some aromatic hydrocarbons to yield molecular compounds or picrates (Procedure 32). The stability

of the picrates varies considerably; many of them dissociate readily into their components. Hence, it is necessary to consult the original literature before preparing such a derivative.

Sulfonamides may also be used to identify aromatic hydrocarbons. The hydrocarbon is converted to the sulfonyl chloride by the action of chlorosulfonic acid (Procedure 37). The sulfonyl chloride is treated with ammonia (Procedure 38) or ammonium carbonate in order to obtain the sulfonamide.



Sulfonamides are especially to be recommended for alkylated benzenes.

REFERENCES

- Acetamino and Benzamino Derivatives of Alkylated Benzenes. Ipatieff and Schmerling, *J. Am. Chem. Soc.*, **59**, 1056 (1937); **60**, 1476 (1938); **65**, 2470 (1943).
Aroylbenzoic Acids. Underwood and Walsh, *J. Am. Chem. Soc.*, **57**, 940 (1935).
Picrates. Baril and Hauber, *J. Am. Chem. Soc.*, **53**, 1087 (1931).
Sulfonamides. Huntress and Autenrieth, *J. Am. Chem. Soc.*, **63**, 3446 (1941).

PROCEDURE 39

Nitration

The nitration of an aromatic compound, especially if it is an unknown substance, should be carried out with special precautions since many compounds react violently.

A. About 1 g. of the compound is added to 4 ml. of concentrated sulfuric acid. Four milliliters of concentrated nitric acid is added drop by drop, with shaking after each addition. The flask is connected to a reflux condenser and kept in a beaker of water at 45° for 5 minutes. The reaction mixture is poured on 25 g. of cracked ice and the precipitate collected on a filter. It may be recrystallized from dilute ethanol.

B. The procedure outlined above is followed except that 4 ml. of fuming nitric acid is used instead of concentrated nitric acid, and the mixture is warmed on the steam cone for 10 minutes. Occasionally, with compounds which are difficult to nitrate, fuming sulfuric acid may be substituted for the concentrated sulfuric acid.

Discussion. Procedure A yields *m*-dinitrobenzene from benzene or nitrobenzene and the *p*-nitro derivative of chlorobenzene, bromobenzene, benzyl chloride, or toluene. Phenol, acetanilide, naphthalene, and

biphenyl yield dinitro derivatives. It is best to employ procedure B for halogenated benzenes since it produces dinitro derivatives which are easier to purify than the mononitro derivatives formed in procedure A. Mesitylene, the xylenes, and pseudocumene yield trinitro derivatives.

PROCEDURE 40

The Oxidation of a Side Chain

A. Dichromate Oxidation. In a small flask are placed 15 ml. of water, 7 g. of sodium dichromate, and 2 to 3 g. of the compound to be oxidized. Ten milliliters of concentrated sulfuric acid is added, the flask attached to a reflux condenser, and the mixture thoroughly shaken. The flask is heated carefully until the reaction starts; then the flame should be removed and the flask cooled if necessary. After the mixture has ceased to boil from the heat of the reaction it is heated under reflux for 2 hours. The contents of the flask are poured into 25 ml. of water, and the precipitate is collected on a filter. The precipitate is mixed with 20 ml. of 5% sulfuric acid, and the mixture is warmed on a steam cone with vigorous stirring. It is cooled, and the precipitate is separated and washed with 20 ml. of water. The residue is dissolved in 20 ml. of 5% sodium hydroxide solution, and the solution is filtered. The filtrate is poured, with vigorous stirring, into 25 ml. of 10% sulfuric acid. The precipitate is collected on a filter and washed with water, and purified by recrystallization from ethanol or benzene.

B. Permanganate Oxidation. One gram of the compound is added to 80 ml. of water containing 4 g. of potassium permanganate. One milliliter of 10% sodium hydroxide solution is added, and the mixture is heated under reflux until the purple color of the permanganate has disappeared ($\frac{1}{2}$ to 3 hours). At the end of this time the mixture is allowed to cool and is acidified carefully with sulfuric acid. The mixture is heated for $\frac{1}{2}$ hour and cooled. Any excess manganese dioxide is removed by the addition of a little sodium bisulfite solution. The precipitated acid is collected on a filter and recrystallized from benzene or ethanol. Occasionally it may be necessary to extract the acid from the solution by means of benzene or ether.

PROCEDURE 41

Aroylbenzoic Acids

To a solution of 1 g. of the dry aromatic hydrocarbon and 1.2 g. of phthalic anhydride in 10 ml. of dry carbon disulfide is added 2.4 g. of anhydrous aluminum chloride. The mixture is heated under a reflux

condenser in a boiling water bath for 30 minutes and cooled. The carbon disulfide layer is decanted, and 10 ml. of concentrated hydrochloric acid and 10 ml. of water are added to the residue. The acid should be added slowly at first, with cooling by ice if necessary, and the final mixture should be thoroughly shaken. If the aroylbenzoic acid separates as a solid, it is immediately collected on a filter and washed with cold water. If an oil separates, the mixture is cooled in an ice bath for some time in order to induce crystallization. If the product remains oily, the supernatant liquid is decanted and the oil is washed with cold water. The crude product, whether a solid or an oil, is boiled for 1 minute with 30 ml. of 10% ammonium hydroxide solution to which has been added about 0.1 g. of Norite. The hot solution is filtered and cooled; 25 g. of crushed ice is then added, and the solution is acidified with concentrated hydrochloric acid. The aroylbenzoic acid is removed by filtration and is recrystallized from dilute ethanol (30 to 80%). Sometimes it is necessary to allow the product to stand overnight in order to obtain crystals.

HYDROCARBONS—PARAFFINS AND CYCLOPARAFFINS

(Listed on p. 260)

Derivatives suitable for identification work have not been developed for these compounds. It is necessary, therefore, to base the identification on physical constants. The most useful of these are boiling point, specific gravity, and refractive index.

REFERENCES

- International Critical Tables.*
Doss, *Physical Constants of the Principal Hydrocarbons*, The Texas Co., New York, 1939.
Egloff, *Physical Constants of Hydrocarbons*, Vols. I and II, Reinhold Publishing Corporation, New York, 1939.

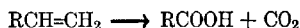
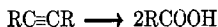
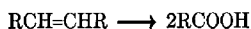
HYDROCARBONS—UNSATURATED

(Listed on p. 261)

Many simple olefinic hydrocarbons may be identified by means of physical constants. In some cases addition compounds with bromine (Procedure 29), hydrogen halides, or nitrosyl chloride furnish solid derivatives. The last-named reagent has found special application to the terpenes.¹

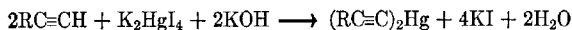
¹ See Simonsen, *The Terpenes*, Vols. I and II, Cambridge University Press, 1931.

Oxidation of a symmetrically substituted olefin or acetylene, a 1-alkene, or a 1-alkyne produces an acid. The oxidation is usually effected by permanganate (Procedure 40B).

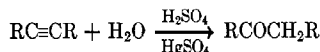


If the acid is a solid it will serve as a derivative. If it is a liquid it may be characterized by means of a suitable derivative (Procedures 1, 2, 3).

Acetylenic compounds containing the grouping $\text{-C}\equiv\text{CH}$ form mercury derivatives which are suitable for identification purposes.



Disubstituted acetylenes may be hydrated to ketones by the action of sulfuric acid and mercuric sulfate in dilute alcoholic solutions.

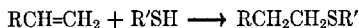


The ketone may then be characterized by a suitable carbonyl reagent (Procedures 13, 14, 15, 42).

Mercaptans and thiophenols condense with olefins to produce the corresponding sulfides.

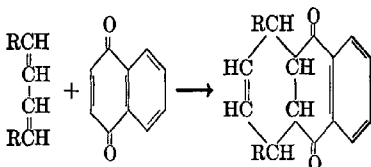


The reaction proceeds according to Markownikoff's rule if acids are present as catalysts. In the presence of peroxides the mode of addition may be reversed.



Although most sulfides are liquids, they may be identified with reference to the sulfones which they give when oxidized. The sulfones are solids and are easily purified.

Hydrocarbons containing conjugated double bonds readily condense with maleic anhydride or α -naphthoquinone to give solid derivatives.



REFERENCES

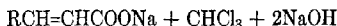
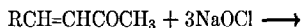
- Mercury Derivatives of Acetylenic Hydrocarbons.** Johnson and McEwen, *J. Am. Chem. Soc.*, **48**, 469 (1926).
Maleic Anhydride Addition Compounds. Diels and Alder, *Ber.*, **62**, 2081 (1929).
 α -Naphthoquinone Addition Compounds. Diels and Alder, *Ber.*, **62**, 2337 (1929).
Olefins and Thiophenol. Ipatieff, Pines, and Friedman, *J. Am. Chem. Soc.*, **60**, 2731 (1938); Ipatieff and Friedman, *ibid.*, **61**, 71, 684 (1939).
Olefins and Mercaptans. Jones and Reid, *J. Am. Chem. Soc.*, **60**, 2452 (1938).
Hydration of Acetylenes. Johnson, Schwartz, and Jacobs, *J. Am. Chem. Soc.*, **60**, 1882 (1938); Thomas, Campbell, and Hennion, *ibid.*, **60**, 718 (1938).
Dithiocyanates from Olefins. Derner and Dysinger, *J. Am. Chem. Soc.*, **61**, 750 (1939).

KETONES

(Listed on p. 262)

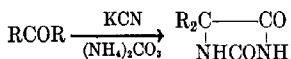
The carbonyl reagents described under aldehydes (pp. 167-168) may be used to obtain solid derivatives of ketones. Low-molecular-weight ketones may be characterized by means of 2,4-dinitrophenylhydrazones (Procedure 15), *p*-nitrophenylhydrazones (Procedure 14), or semicarbazones (Procedure 13A, 13B). For the higher-molecular-weight ketones, hydrazones, phenylhydrazones (Experiment 23, p. 116), and oximes (Procedure 42) are suitable.

Methyl ketones may be oxidized to acids selectively by means of sodium hypochlorite. This reagent is particularly useful for unsaturated methyl ketones since ordinary oxidizing agents attack the double bond.



Hydantoin, formed by warming the carbonyl compound with a mixture of potassium (or sodium) cyanide and ammonium car-

bonate, have been recommended as derivatives, especially for keto ethers.



REFERENCES

See references under aldehydes on page 168.

Reaction of Methyl Ketones with Hypochlorite. VanArendonk and Cupery, *J. Am. Chem. Soc.*, **53**, 3184 (1931); Hurd and Thomas, *ibid.*, **55**, 1646 (1933).

Oximes. Houben and Pfankuch, *Ber.*, **59**, 2392 (1926); Buck and Ide, *J. Am. Chem. Soc.*, **53**, 1536 (1931); Bryant and Smith, *ibid.*, **57**, 57 (1935); Bachmann and Boatner, *ibid.*, **58**, 2097 (1936); Bachmann and Barton, *J. Org. Chem.*, **3**, 300 (1938).

Hydantoins. Henze and Speer, *J. Am. Chem. Soc.*, **64**, 522 (1942).

PROCEDURE 42

Oximes

A. Pyridine Method. A mixture of 1 g. of the aldehyde or ketone, 1 g. of hydroxylamine hydrochloride, 5 ml. of pyridine, and 5 ml. of absolute ethanol is refluxed for 2 hours on a steam bath. The solvents are removed by evaporation in a current of air under a hood. The residue is triturated thoroughly with 5 ml. of cold water, and the mixture is filtered. The oxime is recrystallized from methanol, ethanol, or an ethanol-water mixture.

B. About 0.5 g. of hydroxylamine hydrochloride is dissolved in 3 ml. of water; 2 ml. of 10% sodium hydroxide solution and 0.2 g. of the aldehyde or ketone are then added. If the carbonyl compound is water insoluble just sufficient ethanol is added to the mixture to give a clear solution. The mixture is warmed on the steam bath for 10 minutes and cooled in an ice bath. In order to hasten crystallization the sides of the flask are scratched with a glass rod. Occasionally the addition of a few milliliters of distilled water will assist in causing the oxime to separate. The product may be recrystallized from water or dilute ethanol.

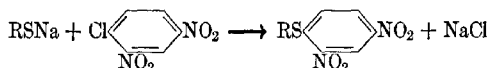
Certain cyclic ketones, such as camphor, require an excess of alkali and longer time of heating. If a ketone fails to yield an oxime by either of the above methods, 1 g. of it should be treated with 1 g. of hydroxylamine hydrochloride, 4 g. of potassium hydroxide, and 20 ml. of 95% ethanol. The mixture is refluxed for 2 hours and poured into 150 ml. of water. The suspension is stirred and allowed to stand to permit un-

changed ketone to separate. The solution is filtered, acidified with hydrochloric acid, and allowed to stand to permit the oxime to crystallize. The product is recrystallized from ethanol or an ethanol-water mixture.

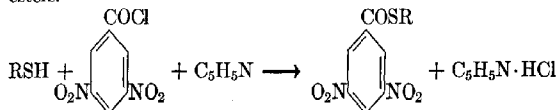
MERCAPTANS

(Listed on p. 266)

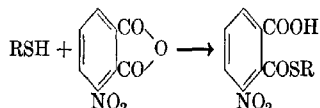
Mercaptans and thiophenols may be converted to the 2,4-dinitrophenyl thio ethers by reaction with 2,4-dinitrochlorobenzene.



3,5-Dinitrobenzoyl chloride may be used to prepare the thio esters.



Mercaptans also react with 3-nitrophthalic anhydride.



The mercury derivatives have been used for characterization but are not as good as the other derivatives mentioned.

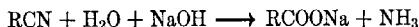
REFERENCES

- 2,4-Dinitrophenyl Thio Ethers.** Bost, Turner, and Norton, *J. Am. Chem. Soc.*, **54**, 1985 (1932).
3,5-Dinitrothiobenzoates and 3-Nitrothiophthalates. Wertheim, *J. Am. Chem. Soc.*, **51**, 3661 (1929).
Anthraquinone Thio Ethers and Sulfones. Reid, Mackall, and Miller, *J. Am. Chem. Soc.*, **43**, 2104 (1921); Hoffman and Reid, *ibid.*, **45**, 1831 (1923); Ellis and Reid, *ibid.*, **54**, 1674 (1932).

NITRILES

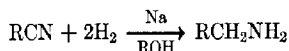
(Listed on p. 267)

The nitriles may be hydrolyzed to the corresponding acids by means of acids (Procedure 43) or alkalies (Experiment 28, p. 128).

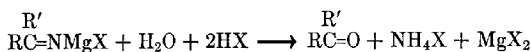
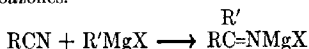


If the resulting acid is a solid it serves as an excellent derivative. If the acid is a liquid or is water soluble it is difficult to separate in pure form and is best characterized by means of its *p*-bromophenacyl ester (Procedure 1). For data on the acids and their derivatives see Table XIX.

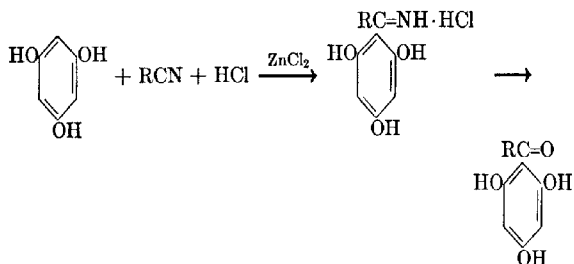
Reduction of nitriles with sodium and an alcohol forms primary amines (Procedure 44), which may be identified by direct conversion to substituted phenylthioureas.



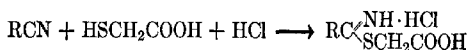
Treatment of the nitriles with the Grignard reagent and subsequent hydrolysis produce ketones which can be characterized by their semicarbazones.



The Hoesch reaction may also be used for the identification of nitriles. Phloroglucinol is used as the phenol in order to obtain the solid alkyl trihydroxyphenyl ketones.



Mercaptoacetic acid (thioglycolic acid) condenses with nitriles in the presence of hydrogen chloride to produce α -iminoalkylmercaptoacetic acid hydrochlorides (Procedure 45).



These salts may be characterized by their decomposition points and neutralization equivalents. They act as dibasic acids when titrated with alkali, thymol blue being used as the indicator.

All these methods involve addition to the cyano group and fail with *ortho* substituted benzonitriles such as *o*-tolunitrile or *o*-chlorobenzonitrile. Sterically hindered nitriles may be hydrolyzed to acids by heating with 75% sulfuric acid (Procedure 43).

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- Alkyl Phenyl Ketones.** Shriner and Turner, *J. Am. Chem. Soc.*, **52**, 1267 (1930).
Alkyl 2,4,6-Trihydroxyphenyl Ketones. Howells and Little, *J. Am. Chem. Soc.*, **54**, 2451 (1932).
 α -Iminoalkylmercaptoacetic Acid Hydrochlorides. Condo, Hinkel Fassero, and Shriner, *J. Am. Chem. Soc.*, **59**, 230 (1937).
Reduction of Nitriles and Formation of Substituted Phenylthioureas. Cutter and Taras, *Ind. Eng. Chem., Anal. Ed.*, **13**, 830 (1941).

PROCEDURE 43

Acid Hydrolysis of Nitriles

About 25 ml. of 75% sulfuric acid and 1 g. of sodium chloride are placed in a 100-ml. round-bottomed flask fitted with a reflux condenser. The flask is heated to 150–160° by means of an oil bath, and 5 g. of the nitrile is added in 0.5-ml. portions through the top of the condenser, with vigorous shaking after the addition of each portion. The mixture is heated, with stirring, at 160° for 30 minutes and at 190° for another ½ hour. It is then cooled and poured on 100 g. of cracked ice in a beaker, and the precipitate is collected on a filter. The precipitate is treated with a slight excess of 10% sodium hydroxide solution, and any insoluble amide is removed by filtration. Acidification of the filtrate yields the organic acid, which may be purified by recrystallization from benzene or an acetone-water mixture.

Hydrochloric acid is more effective than sulfuric for many nitriles.¹ However, for nitriles that are difficult to hydrolyze it is advisable to choose sulfuric acid because of its higher boiling point. The addition of a small amount of hydrochloric acid (as sodium chloride) increases the rate of the reaction.

PROCEDURE 44

Reduction of Nitriles to Amines and Conversion to Substituted Phenylthioureas

In a clean, dry, 200-ml., round-bottomed flask, fitted with a reflux condenser, are placed 20 ml. of absolute ethanol and 1 g. of an aliphatic nitrile (or 2 g. of an aromatic nitrile). Through the top of the condenser 1.5 g. of finely cut sodium slices is added as rapidly as possible without causing the reaction to become too vigorous. When the reduction is complete (10–15 minutes), the mixture is cooled to 20°, and 10 ml. of concentrated hydrochloric acid is added through the condenser, dropwise and with vigorous swirling of the contents of the flask. The reaction mixture is tested to make certain that it is acid to litmus and transferred to a 200-ml. distilling flask connected to a condenser. About 20 ml. of ethanol and water is removed by distillation. The flask and contents are cooled, and a small dropping funnel containing 15 ml. of 40% sodium hydroxide solution is fitted to the top of the distilling flask. An adapter is attached to the end of the condenser and arranged so that it dips into 3 ml. of water in a 50-ml. Erlenmeyer flask. The alkali is added drop by drop, with shaking. The reaction is vigorous, and care must be exercised to avoid adding the alkali too fast. After all the alkali has been added, the mixture is heated until the distillation of the amine is complete. Distillation is stopped when the contents of the flask are very viscous.

To the distillate is added 0.5 ml. of phenyl isothiocyanate, and the mixture is shaken very vigorously for 3–5 minutes. If the derivative does not separate immediately, crystallization is induced by cooling the flask in an ice bath and scratching the walls. The precipitate is collected on a filter, washed with a little cold 50% ethanol, and recrystallized twice from a hot ethanol-water mixture.

PROCEDURE 45

α -Iminoalkylmercaptoacetic Acid Hydrochlorides

One gram of the nitrile and 2.0 g. of mercaptoacetic acid (thioglycolic acid) are dissolved in 15 ml. of absolute ether in a clean dry test tube.

¹ Kilpatrick, *J. Am. Chem. Soc.*, **69**, 40 (1947).

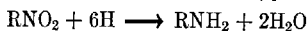
The solution is cooled in an ice bath and thoroughly saturated with dry hydrogen chloride. The tube is tightly stoppered and kept in the ice bath or refrigerator until crystals of the derivative separate. Aliphatic nitriles form the addition compound in 15 to 30 minutes whereas aromatic nitriles usually have to stand overnight in a refrigerator.

The crystals are removed by filtration, washed thoroughly with absolute ether, and placed in a vacuum desiccator containing concentrated sulfuric acid in the bottom and small beakers of potassium hydroxide pellets and paraffin wax in the top. The decomposition point is determined in the usual melting-point apparatus and, if necessary, the neutralization equivalent by titration with standard alkali, thymol blue being used as the indicator.

NITRO COMPOUNDS

(Listed on p. 268)

The reduction of nitro compounds in acidic media leads to the formation of primary amines (Experiment 32, p. 144).



These may be converted into suitable derivatives such as the *N*-substituted benzamides, acetamides, and arylsulfonamides.

Aromatic mononitro compounds may often be characterized by conversion to the corresponding dinitro or trinitro derivatives (Procedures 39A and 39B). Many polynitro aromatic compounds form characteristic addition compounds with naphthalene.

In some cases bromination of the ring (Procedure 29) or oxidation of an alkyl side chain (Procedures 40A and 40B) offers the most suitable means of obtaining a derivative.

The nitroparaffins may be characterized by reduction with zinc and hydrochloric acid to the corresponding primary amines, which may then be converted to solid derivatives by reaction with phenyl isothiocyanate, ethyl oxalate, or 2,4-dinitrochlorobenzene. The sodium salts of aliphatic nitro compounds will also couple with aryldiazonium salts, and in some cases the resulting compounds are solids which may serve as derivatives.

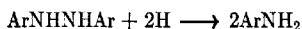
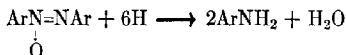
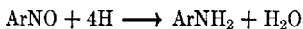
REFERENCES

- Molecular Compounds of Polynitro Aromatic Compounds with Naphthalene.** Dermer and Smith, *J. Am. Chem. Soc.*, **61**, 748 (1939).
Nitroparaffin Derivatives. Dermer and Hutcheson, *Proc. Okla. Acad. Sci.*, **23**, 60 (1943); *C. A.*, **38**, 2006 (1944).

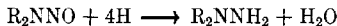
NITROSO, AZOXY, AZO, AND HYDRAZO COMPOUNDS

(Listed on p. 270)

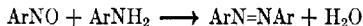
Nitroso, azoxy, azo, and hydrazo compounds may be reduced by tin and hydrochloric acid (Experiment 32, p. 144) to the corresponding amines.



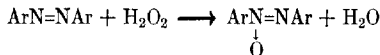
The amines are characterized by conversion to suitable acyl derivatives. Nitrosamines undergo reduction to substituted hydrazines.



Occasionally special reactions may be used. For example, nitroso compounds may be condensed with primary amines to yield azo compounds.

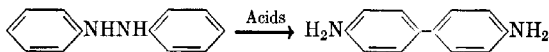


Azo compounds may be oxidized to azoxy compounds by hydrogen peroxide.



Azoxy compounds may be reduced to azo compounds by suitable reagents.

The hydrazo compounds may be acetylated, benzoylated, or caused to undergo rearrangement.

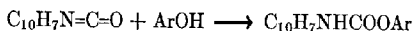


PHENOLS

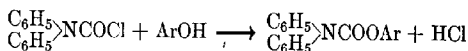
(Listed on p. 271)

Phenols, like the alcohols, yield urethans when treated with isocyanates (Procedure 48). Among the latter α -naphthyl isocyanate is perhaps the most generally useful reagent for identifying

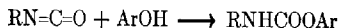
phenols (Procedure 6A). This reaction is catalyzed by the addition of a few drops of dry pyridine.¹



Another type of urethan which is often used is the diphenylurethan; it is derived from diphenylcarbonyl chloride, $(\text{C}_6\text{H}_5)_2\text{NCOCl}$, according to the following equation (Procedure 6B).

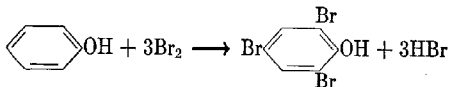


Urethans may also be obtained by treating acid azides with the phenol. The acid azide decomposes into nitrogen and the isocyanate, which then reacts with the phenol.



By this means β -naphthylurethans as well as *p*-chloro-, *p*-bromo-, *p*-nitro-, 3,5-dinitro-, and 3,5-dinitro-4-methylphenylurethans have been made.

A majority of the phenols can be identified readily by reference to their bromination products (Procedure 47). Thus phenol reacts with bromine to give 2,4,6-tribromophenol.



In the presence of alkali, phenols react readily with chloroacetic acid to give aryloxyacetic acids. These derivatives crystallize well from water and have proved to be exceedingly useful in characterization work (Procedure 46).



The aryloxyacetic acids can be compared not only by melting-point determinations but also by reference to their neutralization equivalents.

Other types of derivatives of phenols which are used frequently are the nitro derivatives (Procedure 39A), picrates (Procedures 23A and 23B), acetates (Procedures 18A and 18B), 3,5-dinitrobenzoates (Procedure 9), and sulfonic acid esters.

¹ Tarbell, Mallatt, and Wilson, *J. Am. Chem. Soc.*, **64**, 2229 (1942).

O-Alkylsaccharin derivatives, which were discussed in connection with alcohols (p. 161), can be used also in identifying phenols.

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Aryloxyacetic Acids. Koelsch, *J. Am. Chem. Soc.*, **53**, 304 (1931); Hayes and Branch, *ibid.*, **65**, 1555 (1943).
Sulfonic Acid Esters. Sekera, *J. Am. Chem. Soc.*, **55**, 421 (1933).
Picrates. Baril and Hauber, *J. Am. Chem. Soc.*, **53**, 1087 (1931).
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p-Nitrobenzyl Ethers. Reid, *J. Am. Chem. Soc.*, **39**, 304 (1917); Lyman and Reid, *ibid.*, **42**, 615 (1920).
3,5-Dinitrophenylurethans. Sah and Ma, *J. Chinese Chem. Soc.*, **2**, 229 (1934).
Phenylurethans. McKinley, Nickels, and Sidhu, *Ind. Eng. Chem., Anal. Ed.*, **16**, 304 (1944).
n-Naphthylurethans. French and Wirtel, *J. Am. Chem. Soc.*, **48**, 1736 (1926).
2,4-Dinitrophenyl Ethers. Bost and Nicholson, *J. Am. Chem. Soc.*, **57**, 2368 (1935).
p-Chlorophenylurethans. Kao, Fang, and Sah, *Science Repts., Natl. Tsinghua Univ.*, (A)3, 109 (1935).
β-Naphthylurethans. Sah, *Rec. trav. chim.*, **58**, 453 (1939).
p-Nitrophenylurethans. Sah and Chiao, *Rec. trav. chim.*, **58**, 595 (1939).
p-Bromophenylurethans. Sah and Cheng, *Rec. trav. chim.*, **58**, 591 (1939).
3,5-Dinitro-4-methylphenylurethans. Sah, *Rec. trav. chim.*, **58**, 582 (1939).

PROCEDURE 46

Aryloxyacetic Acids

To a mixture of 1 g. of the phenol with 5 ml. of a 33% sodium hydroxide solution is added 1.5 g. of chloroacetic acid. The mixture is shaken thoroughly, and 1 to 5 ml. of water may be added if necessary in order to dissolve the sodium salt of the phenol. The test tube containing the mixture is then kept in a beaker of boiling water for 1 hour. The solution is cooled, diluted with 10 to 15 ml. of water, acidified to Congo red with dilute hydrochloric acid and extracted with 50 ml. of ether. The ether solution is washed with 10 ml. of cold water and is then shaken with 25 ml. of 5% sodium carbonate solution. The sodium carbonate solution is acidified with dilute hydrochloric acid; the aryloxyacetic acid is then collected on a filter and recrystallized from hot water.

PROCEDURE 47

Bromination of Phenols

A brominating solution is prepared by dissolving 15 g. of potassium bromide in 100 ml. of water and adding 10 g. of bromine. This solution is added slowly, with shaking, to a solution of 1 g. of the phenol dissolved in water, ethanol, acetone, or dioxane. Just enough of the brominating solution is added to impart a yellow color to the mixture. About 50 ml. of water is then added, and the mixture is shaken vigorously to break up the lumps. The bromo derivative is removed by filtration and washed with a dilute solution of sodium bisulfite. It is recrystallized from ethanol or a water-ethanol mixture.

PROCEDURE 48

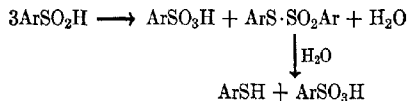
Phenylurethans

To a mixture of 0.5 g. of the dry phenol and 0.5 ml. of phenyl isocyanate in a dry 25-ml. flask is added 1 drop of dry pyridine. The flask is loosely stoppered with a plug of cotton and heated on a steam cone for 15 minutes. If separation of the derivative does not occur during this time, crystallization is induced by cooling the flask and scratching the walls. When crystals have formed, 10 ml. of dry benzene (or dry ethyl acetate) is added. The mixture is heated on a steam cone and filtered through a fluted filter. Hexane is now added until a turbidity or crystals are obtained. Crystallization is allowed to proceed overnight; the product is then removed by filtration, washed with hexane containing a little benzene, and air dried.

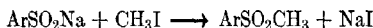
If any water is present in the original sample or reagents, the product will be contaminated with *s*-diphenylurea; m.p. 238°. Purification may be effected by warming the product with 10 ml. of carbon tetrachloride and removing the insoluble diphenylurea by filtration. The phenylurethan may be obtained by cooling the filtrate. Occasionally the filtrate may have to be evaporated to 2 to 3 ml. to cause the crystallization to occur.

SULFINIC ACIDS AND SALTS OF SULFINIC ACIDS

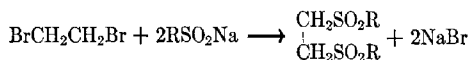
A number of aromatic sulfinic acids have been prepared, but the free acids are unstable, changing to the corresponding sulfonic acids and thiosulfonates. The thiosulfonates undergo hydrolysis to yield thiophenols and sulfonic acids.



Aliphatic sulfinic acids are less stable than aromatic; hence both types usually are met as the sodium, potassium, or magnesium salts, which are more stable. The best derivatives are those produced by alkylation, which forms sulfones rather than esters. Methyl iodide, for example, reacts with sodium arylsulfonates to yield methyl sulfones.



Ethylene bromide has been used to prepare solid 1,2-dialkylsulfonylethanes from salts of aliphatic sulfinic acids.



The sodium salts of aryl- and alkylsulfonates react with mercuric chloride to form the corresponding aryl- and alkylmercuric chlorides, which are crystalline solids.

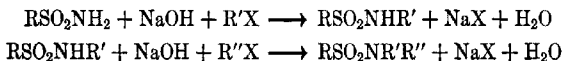
REFERENCES

- 1,2-Dialkylsulfonylethanes.** Allen, *J. Org. Chem.*, **7**, 23 (1942).
Aryl- and Alkylmercuric Chlorides from Sulfonates. Peters, *Ber.*, **38**, 2567 (1905); Kharasch and Chalkley, *J. Am. Chem. Soc.*, **43**, 607 (1921); Whitmore, Hamilton, and Thurman, *J. Am. Chem. Soc.*, **45**, 1066 (1923); Coffey, *J. Chem. Soc.*, **1926**, 637; Marvel, Adams, and Johnson, *J. Am. Chem. Soc.*, **68**, 2735 (1946).

SULFONAMIDES

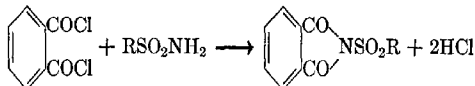
(Listed on p. 273)

Sulfonamides which have at least one hydrogen atom on the nitrogen atom can be alkylated by treatment of the sodium salts with reactive halides or alkyl sulfates.

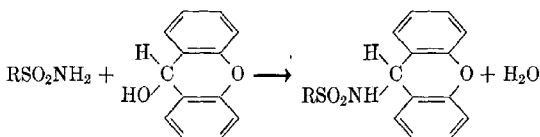


These reactions are useful if the alkyl group is so chosen that a known sulfonamide is produced.

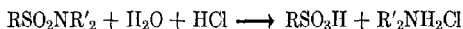
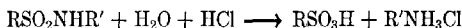
Primary sulfonamides react with phthalyl chloride to produce *N*-sulfonylphthalimides.



Primary amides of sulfonic acids, like those of carboxylic acids (p. 173), react with xanthydrol to form *N*-xanthylsulfonamides, which are satisfactory derivatives (Procedure 49).



Sulfonamides are hydrolyzed by refluxing with 25% hydrochloric acid (p. 92).



The amine may be separated by the addition of alkali and characterized by a suitable derivative (p. 174). If necessary the sulfonic acid may be recovered in the form of its sodium salt (after removal of the amine) and converted to a derivative (Procedure 51 or 52).

REFERENCE

N-Xanthylsulfonamides. Phillips and Frank, *J. Org. Chem.*, **9**, 9 (1944).

PROCEDURE 49

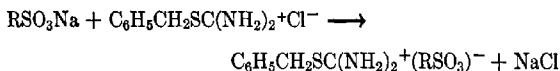
N-Xanthylsulfonamides

About 0.2 g. of xanthydrol is dissolved in 10 ml. of glacial acetic acid. If the mixture is not clear, it is filtered or centrifuged, and to the clear solution is added 0.2 g. of the sulfonamide. The mixture is shaken and allowed to stand at room temperature until the derivative separates; this may require as long as 1.5 hours. The *N*-xanthylsulfonamide is removed by filtration and recrystallized from a dioxane-water mixture (3:1).

SULFONIC ACIDS AND SALTS OF SULFONIC ACIDS

(Listed on p. 275 under sulfonyl chlorides)

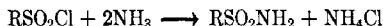
Sulfonic acids and their salts, like carboxylic acids and their salts, readily form characteristic derivatives with *S*-benzylthiuronium chloride. This reaction represents the shortest and most direct method for obtaining derivatives of these compounds (Procedure 50).



Sulfonic acids and their salts are converted into sulfonyl chlorides by heating with phosphorus pentachloride (Procedure 51).

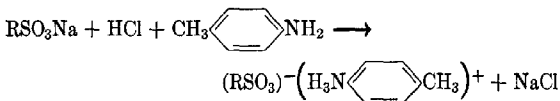


The chloride is then treated with ammonia or an amine to obtain the amide (Procedures 31, 51).



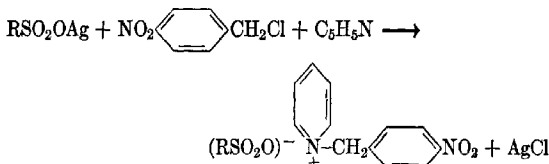
Since the sulfonic acids are strong it is not possible to obtain them by acidification of their salts unless the sulfonic acid is very insoluble in water or hydrochloric acid. Sulfonic acids combine with amines to produce salts which have definite melting or decomposition points and hence may be used as derivatives.

By treating a concentrated solution of a sodium salt of a sulfonic acid with hydrochloric acid and *p*-toluidine it is possible to cause the *p*-toluidine salts to separate (Procedure 52). These are useful derivatives.



The phenylhydrazine salts are useful for aliphatic sulfonic acids.

When silver sulfonates are allowed to react with *p*-nitrobenzyl chloride and pyridine the corresponding *p*-nitrobenzylpyridinium salts are formed.



These salts crystallize readily, have sharp and characteristic melting points, and are suitable as derivatives. Amino sulfonic acids in the benzene and naphthalene series may be characterized by replacement of the amino group by chlorine through the Sandmeyer reaction, followed by conversion of the sulfonic acid to a sulfonamide or sulfonanilide (Procedure 53).

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***p*-Toluidine Salts of Sulfonic Acids.** Fieser, *Org. Syntheses, Coll. Vol. 2*, 482; *J. Am. Chem. Soc.*, **61**, 2460, 2471 (1929).
***p*-Toluidine Salts of Monoarylsulfates.** Barton and Young, *J. Am. Chem. Soc.*, **65**, 294 (1943).
Phenylhydrazine Salts of Sulfonic Acids. Latimer and Böst, *J. Am. Chem. Soc.*, **59**, 2500 (1937).
***p*-Nitrobenzylpyridinium Salts of Aromatic Sulfonic Acids.** Huntress and Foote, *J. Am. Chem. Soc.*, **64**, 1017 (1942).
Chloroarylsulfonamides and Chlorosulfonanilides. Allen and Frame, *J. Org. Chem.*, **7**, 15 (1942).

PROCEDURE 50

Benzylthiuronium Sulfonates

About 1 g. of the sodium or potassium salt of the sulfonic acid is dissolved in the smallest amount of water, heat being used if necessary to effect solution. If the free sulfonic acid is the starting material, it is dissolved in 2 *N* sodium hydroxide solution, and any excess alkali is neutralized with hydrochloric acid, phenolphthalein being employed as the indicator.

A solution of 1 g. of benzylthiuronium chloride is dissolved in the smallest possible amount of water. This solution and that of the sulfonate are chilled in an ice-water bath, mixed, and shaken thoroughly. Occasionally it is necessary to scratch the tube and cool in an ice bath to induce crystallization. The benzylthiuronium sulfonate crystals are collected

on a filter, washed with a little cold water, and recrystallized from hot 50% ethanol.

PROCEDURE 51

Sulfonyl Chlorides and Sulfonamides from Salts of Sulfonic Acids

Two grams of the salt is mixed with 5 g. of phosphorus pentachloride in a clean, dry flask. A reflux condenser is attached, and the flask is heated in an oil bath at 150° for 30 minutes. The mixture is cooled, and 20 ml. of dry benzene is added. The mixture is then warmed on the steam cone, the solid mass being stirred thoroughly. The solution is filtered through a dry filter paper and the filtrate washed with two 15-ml. portions of water. The benzene is removed by distillation from a steam bath. The residual sulfonyl chloride may be recrystallized from petroleum ether or chloroform. Since the sulfonyl chlorides usually are low-melting compounds it is best to prepare the amide by adding the benzene solution to 20 ml. of concentrated ammonia, with vigorous stirring. Occasionally the sulfonamide precipitates and may be removed by filtration; otherwise it is obtained by evaporation of the benzene layer. The sulfonamides may be recrystallized from ethanol.

PROCEDURE 52

p-Toluidine Salts of Sulfonic Acids

A. From Free Sulfonic Acids. One gram of the sulfonic acid is dissolved in the minimum amount of boiling water and 1 g. of *p*-toluidine added. More water or an additional portion of the sulfonic acid is added to obtain a clear solution. The solution is cooled and the flask scratched to induce crystallization of the salt. The salt is removed by filtration and recrystallized from the minimum amount of boiling water.

B. From Soluble Salts of Sulfonic Acids. About 2 g. of the sodium, potassium, or ammonium salt of the sulfonic acid is dissolved in the minimum amount of boiling water, and 1 g. of *p*-toluidine and 2 to 4 ml. of concentrated hydrochloric acid are added. If a precipitate separates or if the *p*-toluidine is not completely dissolved, more hot water and a few drops of concentrated hydrochloric acid are added until a clear solution is obtained at the boiling point. The solution is cooled, and the walls of the flask are scratched to induce crystallization of the salt. The product is removed by filtration and recrystallized from a small amount of water or dilute ethanol.

PROCEDURE 53

**Chloroarylsulfonamides and Chloroarylsulfonanilides from
Aminosulfonic Acids**

About 1.5 g. of the aminoarylsulfonic acid is dissolved in 10 ml. of water containing 0.5 g. of sodium carbonate. Diazotization is effected by adding 2 ml. of concentrated hydrochloric acid and then, quickly, about 5 ml. of 10% sodium nitrite solution, the temperature being maintained at 10–15° by the addition of ice.

Meanwhile, cuprous chloride is prepared by mixing a solution of 2.16 g. of copper sulfate and 0.56 g. of sodium chloride in 10 ml. of water with a solution of 0.46 g. of sodium bisulfite and 0.33 g. of sodium hydroxide in 10 ml. of water. The precipitated cuprous chloride is then dissolved in 10 ml. of concentrated hydrochloric acid. The solution is cooled in ice to 5°, and the diazonium solution is added rapidly, with stirring. The temperature is allowed to rise slowly to room temperature, stirring being continued for 1 hour, and the solution is then heated to 60–70° for 30 minutes on the steam bath. The copper is precipitated by hydrogen sulfide, and the resulting copper sulfide is removed by filtration. The crude chloroarylsulfonic acid is obtained by evaporating the filtrate to dryness on the steam bath.

The crude acid is then mixed with double its weight of phosphorus pentachloride in a small beaker. When the vigorous reaction has ended, the beaker is heated for a short time in an oil bath at 130–140° (under a hood) to expel the phosphorus oxychloride. After being cooled, the chloride is washed by decantation with cold water. The resulting oil is added to 45 ml. of concentrated ammonium hydroxide, and the solution is evaporated to dryness on the steam bath. The crude sulfonamide is recrystallized, with the addition of Norite, from ethanol or water.

In order to prepare the chloroarylsulfonanilide, a solution of the crude sulfonyl chloride in 10 ml. of benzene is mixed with 2.5 g. of aniline, and the resulting solution is heated under reflux for 1 hour. It is then concentrated to half its volume and chilled. The solid that separates is collected on a filter, washed thoroughly with warm water, and recrystallized from chlorobenzene.

SULFONYL CHLORIDES

(Listed on p. 275)

Sulfonyl chlorides are readily converted to amides by treatment with aqueous ammonia (Procedure 51) or with ammonium carbonate (Procedure 31). The Hinsberg reaction (Experiment 4, p. 91) serves to produce sulfonanilides or sulfonoluides which are good derivatives.

CHAPTER IX

TABLES OF DERIVATIVES

The tables on the following pages contain common organic compounds arranged according to classes. The compounds in each table are listed in the order of boiling points or melting points. These tables are intended to serve chiefly as a guide in the preparation of the list of possible compounds and to suggest certain derivatives. They are not to be considered an exhaustive summary of the literature. This is particularly true of the derivatives which are listed. These have been chosen primarily to illustrate the procedures in Chapter VIII, and the tables are not necessarily complete even in this respect.

In describing compounds in the literature it is customary, of course, to give a range of a certain number of degrees for the boiling point or melting point. In order to keep the following tables from being too cumbersome, only the highest point of the boiling- or melting-point range is listed; this value is given to the nearest whole degree. Specific gravities are given for a temperature of 20° referred to water at 4° unless otherwise indicated. Refractive indices are given at 20° for the sodium D line.

Students should bear in mind that the value obtained for a melting point depends somewhat on the observer and on the method which was used in the determination. Thus, it often happens that the literature gives several different values for the same constant. In such cases the highest value has generally been chosen for the tables which follow. However, it is obvious that this procedure may lead to serious error. Consequently, if the student encounters any difficulties in using these tables, he should consult the original literature references cited in Chapter VIII for further details.

It has not been possible to incorporate into the tables all the new types of derivatives which have been developed during the

past few years. Hence, the literature references given in Chapter VIII should be consulted for melting points of new derivatives not in the tables.

TABLE XVII
ACETALS (LIQUIDS)

Name of Compound	B. P.	Name of Compound	B. P.
Dimethoxymethane (methylal)	45°	Di- <i>n</i> -propoxymethane	140°
1,1-Dimethoxyethane	64	1,1-Diethoxybutane	143
2-Methyl-1,3-dioxolane	82	1,1-Di- <i>n</i> -propoxyethane	148
Diethoxymethane (ethylal)	89	1,1-Diethoxy-2-chloroethane	157
1,1-Diethoxyethane (acetal)	102	1,1-Diethoxy-2-bromoethane	170
1,3-Dioxane	105	1,1-Di- <i>sec</i> -butoxyethane	171
2-Methyl-1,3-dioxane	110	1,1-Diisobutoxyethane	176
1,1-Diethoxypropane	124	1,1-Diethoxy-2,2-dichloro-ethane	184
1,1-Diethoxy-2-propene	126	1,1-Di- <i>n</i> -butoxyethane	186

TABLE XVIII

ACID HALIDES AND ANHYDRIDES (LIQUIDS)

Name of Compound	B. P.	M. P.	Derivatives	
			Amides	Anilides
Acetyl chloride.....	55°	82°	115°
Oxalyl chloride.....	64	419d.	245
Propionyl chloride.....	80	79	103
Acetyl bromide.....	81	82	115
Isobutyryl chloride.....	92	129	105
<i>n</i> -Butyryl chloride.....	100	115	90
Chloroacetyl chloride.....	105	119	134
Dichloroacetyl chloride.....	107	98	118
Isovaleryl chloride.....	115	135	109
Trichloroacetyl chloride.....	115	141	94
<i>n</i> -Valeryl chloride.....	127	106	63
Chloroacetyl bromide.....	127	119	134
Bromoacetyl chloride.....	127	91	131
Acetic anhydride.....	138	82	115
Bromoacetyl bromide.....	149	91	131
α -Bromopropionyl bromide..	153	123	99
<i>n</i> -Caproyl chloride.....	153	98	95
Propionic anhydride.....	168	79	103
<i>n</i> -Heptoyl chloride.....	176	94	71
Succinyl chloride.....	190d.	16°	242	226
<i>n</i> -Butyric anhydride.....	191	115	90
Benzoyl chloride.....	197	128	160
Phenylacetyl chloride.....	210	154	117
Citraconic anhydride.....	213	7	187d.	175
<i>n</i> -Valeric anhydride.....	215	106	63
Benzoyl bromide.....	218	128	160
<i>p</i> -Chlorobenzoyl chloride	222	16	179	194
<i>m</i> -Chlorobenzoyl chloride....	225	134	122
<i>o</i> -Chlorobenzoyl chloride....	238	-4	142	114
Crotonic anhydride.....	248	160	118
<i>o</i> -Methoxybenzoyl chloride..	254	128	62
<i>n</i> -Heptoic anhydride.....	258	96	71
Phthalyl chloride (<i>sym.</i>)....	276	14	220	169
<i>m</i> -Nitrobenzoyl chloride.....	278	35	143	154

TABLE XVIII—*Continued*

ACID HALIDES AND ANHYDRIDES (SOLIDS)

Name of Compound	M. P.	Derivatives		
		Acid	Amide	Anilide
Palmityl chloride.....	12°	62°	106°	90°
<i>p</i> -Chlorobenzoyl chloride....	16	242	179	194
Succinyl chloride.....	16	188	242	226
<i>o</i> -Nitrobenzoyl chloride....	20	146	174	155
Stearyl chloride.....	22	69	108	33
Anisyl chloride.....	26	184	162	168
<i>m</i> -Nitrobenzoyl chloride....	35	140	143	153
Cinnamoyl chloride.....	36	133	142	153
Benzoic anhydride.....	42	121	128	160
Chloroacetic anhydride.....	45	62	120	134
Maleic anhydride.....	56	130	153	187
Itaconic anhydride.....	68	165d.	192	190
3,5-Dinitrobenzoyl chloride..	74	202	183	234
<i>p</i> -Nitrobenzoyl chloride.....	75	241	201	204
Diphenylcarbamide chloride..	85	189
4-Nitrophthalic anhydride....	119
Succinic anhydride.....	120	188	242
Cinnamic anhydride.....	130	133	142	153
Phthalic anhydride.....	131	184	149
α -Naphthoic anhydride.....	146	162	205	161
1,2-Naphthalic anhydride....	169	175d.	265d.
<i>d</i> -Camphoric anhydride.....	221	187	192	210
2,3-Naphthalic anhydride....	246	241d.
1,8-Naphthalic anhydride....	274
Tetrabromophthalic anhy- dride.....	275	266
Tetraiodophthalic anhy- dride.....	318	327

TABLE XIX
 ACIDS (LIQUIDS)

Name of Acid	B. P.	Derivatives			
		Anilide	<i>p</i> -Tolu- ide	<i>p</i> -Nitro- benzyl Ester	<i>p</i> -Bromo- phenacyl Ester
Thioacetic.....	93°				
Formic.....	101	47°	53°	31°	100°
Acetic.....	118	114	147	78	85
Acrylic.....	140	104	141		
Propionic.....	140	103	124	31	63
Propiolic.....	144d.				
Isobutyric.....	155	105	104		77
Methacrylic.....	163				
<i>n</i> -Butyric.....	163	95	72	35	63
Pivalic.....	164	129	120		76
Pyruvic.....	165d.	104	109		
Crotonic (<i>cis</i>).....	165d.	102	132		82
Ethylmethyllacetic.....	176	110	93		55
Isovaleric.....	176	109	109		68
Chloroacetic.....	185	134			
α -Chloropropionic.....	186	92	124		
<i>n</i> -Valeric.....	186	63	70		75
Dichloroacetic.....	189	118	153		99
Diethylacetic.....	193	124	116		
Isocaproic.....	195	111	63		77
Tiglic.....	198	77			
α -Bromoisobutyric.....	200				
Methoxyacetic.....	203	58			
<i>n</i> -Caproic.....	205	95	75		72
α -Bromopropionic.....	205	99	125		
Ethoxyacetic.....	206		32		105
Bromoacetic.....	208	131	91	88	
α -Bromo- <i>n</i> -butyric.....	217d.	98	92		
<i>n</i> -Heptoic.....	224	71	80		72
α -Ethyl- <i>n</i> -caproic.....	224				
α -Bromoisovaleric.....	230				
Hexahydrobenzoic.....	232	142			
Dibromoacetic.....	234				
<i>n</i> -Caprylic.....	236	57	70		67
α -Bromo- <i>n</i> -caproic.....	240				
Levulinic.....	250d.	102	109	61	84
Pelargonic.....	253	57	84		68
α -Phenylpropionic.....	265				
Capric.....	270	62	78		67
Undecanoic.....	275d.	71	80		68
β -Phenylpropionic.....	280	92		36	
Undecylenic.....	295				

TABLE XIX—Continued

ACIDS (Solids)

Name of Acid	M. P.	Derivatives			
		Anilide	Amide	p-Nitro- benzyl Ester	p-Bromo- phenacyl Ester
Oleic.....	16°	41°	76°	40°
Methacrylic.....	16	106
d-Lactic.....	18	59	74	112
β-Bromoisobutyric.....	22
Thiobenzoic.....	24
α-Bromopropionic.....	24	99	123
Undecylenic.....	24	85
Undecanoic.....	29	71	103	68
Hexahydrobenzoic.....	30	142	186
Capric.....	30	62	108	67
Levulinic.....	33	102	108	61°	84
Pivalic.....	35	129	154	76
β-Chloropropionic.....	42	101
Lauric.....	43	76	98	76
α-Bromoisovaleric.....	44	133
Angelic.....	46	126	128
Dibromoacetic.....	48	156
β-Phenylpropionic (Hydrocinnamic).....	48	92	82	36	104
α-Bromoisobutyric.....	49	148
Bromoacetic.....	50	131	91	88
Elaidic.....	51	93	65
γ-Phenylbutyric.....	52	84
Myristic.....	54	84	102	81
Trichloroacetic.....	57	94	141	80
Margaric.....	60	106	49	83
β-Bromopropionic.....	62	86
Palmitic.....	62	90	106	42	86
Chloroacetic.....	63	134	120
Tiglic.....	64	77	76	64	68
α,β-Dibromopropionic.....	64	130
Cyanoacetic.....	66	198	123
Chaulmoogric.....	68	89	106
Stearic.....	69	93	108	90
Crotonic (trans).....	72	118	160	67	96
Phenylacetic.....	76	117	154	65	89
Glycolic.....	79	96	120	107	138
α-Hydroxyisobutyric.....	79	136	98	80
β-Iodopropionic.....	82	101
Iodoacetic.....	84	143	95
Citraconic.....	91	175	187d.	71
Phenoxyacetic.....	96	99	101	148
Phthalaldehydic.....	97
Glutaric.....	97	224	174	69	137
Homoveratric (anhydrous).....	99	147
L-Malic.....	100	197	{ 102 156 (di) }	124	179
Citric (hydrated).....	100	199	210	102	148
o-Methoxybenzoic.....	100	62	128	113
Oxalic (hydrated).....	101	257	419d.	204	242d.
o-Toluidic.....	102	125	142	91	57
Pimelic.....	105	155	137
Azelaic.....	106	185	175	44	131
m-Toluidic.....	110	125	97	86	108
Ethylmalonic.....	111	150	214	75

TABLES OF DERIVATIVES

TABLE XIX—Continued
ACIDS (SOLIDS)—Continued

Name of Acid	M. P.	Derivatives			
		Anilide	Amide	<i>p</i> -Nitro- benzyl Ester	<i>p</i> -Bromo- phenacyl Ester
<i>β</i> -Benzoylpropionic.....	116°	150°	125°
<i>p</i> -Isopropylbenzoic.....	116	133
<i>dl</i> -Tropic.....	117	169
Benzylmalonic.....	117d.	217	225	119°
<i>dl</i> -Mandelic.....	118	151	133	124
<i>m</i> -Nitrophenylacetic.....	120	110
Benzoic.....	121	160	128	89	119°
Trichlorolactic.....	124	164	145
3-Nitrosalicylic (hydrated).....	125	145
<i>o</i> -Benzoylbenzoic.....	126	195	165	100
<i>γ</i> -Benzoylbutyric.....	127
2,4-Dimethylbenzoic.....	127	179
Maleic.....	130	187	153	89	168
<i>o</i> -(<i>p</i> -Toluy)-benzoic.....	130
2,5-Dimethylbenzoic.....	132	186
Furoic (Pyromucic).....	133	123	141	133	138
Sebacic.....	133	198	210	72	147
<i>d</i> - or <i>l</i> -Mandelic.....	133	122
Cinnamic.....	133	153	147	116	145
<i>α</i> -Naphthylacetic.....	133	155	181
Malonic.....	133d.	224	170	85
Acetonedicarboxylic.....	135d.	135
Acetylsalicylic.....	135	136	138	90
Methylmalonic.....	135d.	182	217
Phenylpropionic.....	136	125	102	83
Glutaconic (<i>cis</i>).....	136	135(mono)
Glutaconic (<i>trans</i>).....	138	{ 167 (mono) 228 (di) }
2,6-Dichlorobenzoic.....	139
<i>o</i> -Chlorobenzoic.....	140	114	139	106	106
<i>m</i> -Nitrobenzoic.....	140	153	142	141	132
<i>meso</i> -Tartaric.....	140	190
Suberic.....	140	187	216	85	144
Furylacrylic.....	141	168
<i>o</i> -Nitrophenylacetic.....	141	161
3-Nitrosalicylic.....	144	145
Diphenylacetic.....	145	180	167
<i>o</i> -Nitrobenzoic.....	146	155	174	112	107
Phthalonic (anhydrous).....	146	{ 176 (mono) 208 (di) }	{ <i>α</i> -179 { <i>β</i> -155 }
<i>p</i> -Hydroxyphenylacetic.....	148	167
<i>o</i> -Bromobenzoic.....	150	141	155	110
Benzilic.....	150	175	154	99	152
Adipic.....	152	235	220	106	154
<i>p</i> -Nitrophenylacetic.....	152	198	207
2,5-Dichlorobenzoic.....	153	155
Citric.....	153	210d.	102	148
<i>m</i> -Bromobenzoic.....	155	146	155	105
2,4,6-Trimethylbenzoic.....	155	188
Salicylic.....	157	134	139	96	140
<i>m</i> -Chlorobenzoic.....	158	122	134	107	116
2,4-Dichlorobenzoic.....	160
<i>o</i> -Iodobenzoic.....	162	142	184	111	110
<i>α</i> -Naphthoic.....	162	161	205	135
Thiosalicylic.....	163
2,3-Dichlorobenzoic.....	164
3,4-Dimethylbenzoic.....	164	130

TABLE XIX—*Continued*
ACIDS (SOLIDS)—*Continued*

Name of Acid	M. P.	Derivatives			
		Anilide	Amide	p-Nitro- benzyl Ester	p-Bromo- phenacyl Ester
4-Nitrophthalic	165°	192°	200d.°		
Itaconic	165d.	190	192 (di)	91°	117°
Mesitylenic	166		133		
Tricarballic	166	252	207d.		138
d-Dibromosuccinic	167				
d- or l-Tartaric	169	180	195	163	216
3,5-Dinitrosalicylic	173				
p-Toluic	177	140	158	104	153
2,4-Cresotic	178				162
Acetylenedicarboxylic	179		294d.		
Veratric (anhydrous)	181	154	164		
p-Fluorobenzoic	182		154		
2,4-Dinitrobenzoic	183		203	142	158
Anisic	184	168	162	132	152
β-Naphthoic	185	173	195		
Acetylanthranilic	185	167	171		
d-Camphoric	187	203	192	66	
Hippuric	187	208	183	136	151
Succinic	188	226	242	88	211
3-Nitroanisic	190	163			
Aconitic	191		250d.	76	186
Protocatechuic	194d.	166	212	188	
m-Nitrocinnamic	199		196	174	173
2-Chloro-3,5-dinitrobenzoic	199				
Fumaric	200	314	270	151	197
	subl.				
m-Hydroxybenzoic	201	155	170	106	176
3,5-Dinitrobenzoic	202	234	183	157	
Mesaconic	202	185	176	134	
d-Tartaric	204		226	147	
p-Coumaric	206		194		
Phthalic	206d.	169	149	165	153
o-Coumaric	207		209d.	152	
Vanillic	207			140	
p-Hydroxybenzoic	213	202	162	198	191
β-Resorcylic	213	127	222	189	
Mucic	213d.			310	225
p-Cyanobenzoic	214	179		189	
Piperic	216			145	
3-Nitrophthalic	218	234	201	189	
2,4,6-Trinitrobenzoic	220d.		264d.		
2-Hydroxy-3-naphthoic	222	249	218		
5-Nitrosalicylic	227	224	225		
Methyliminodiacetic	227d.		169		
Diphenic	228	230	212	183	
Piperonylic	229		169		
o-Nitrocinnamic	240		185	132	141
Gallie	240d.	207	245		
p-Nitrobenzoic	241	204	201	168	137
p-Chlorobenzoic	242	194	179	129	
Tetrachlorophthalic	250d.			180	
p-Bromobenzoic	251	197	189	139	
Chelidonic	262				
p-Iodobenzoic	265	210	217	141	147
p-Nitrocinnamic	285		204	186	
Mellitic	288d.				
Isophthalic	300		280	215	186
Terephthalic	300	337		263	225
	subl.				
Trimesic	350	120d.	365d.		197

TABLE XX
ALCOHOLS (LIQUIDS)

Name of Compound	B. P.	Derivatives		
		α -Naphthyl- urethan	Phenyl- urethan	3,5-Dinitro- benzoate
Methyl alcohol.....	66°	124°	47°	107°
Ethyl alcohol.....	78	79	52	93
Isopropyl alcohol.....	83	106	88	122
<i>tert</i> -Butyl alcohol.....	83	101	136	142
Allyl alcohol.....	97	109	70	48
<i>n</i> -Propyl alcohol.....	97	80	51	74
<i>sec</i> -Butyl alcohol.....	99	97	65	75
<i>tert</i> -Amyl alcohol.....	102	71	42	117
Isobutyl alcohol.....	108	104	86	86
Methylisopropylcarbinol.....	113	112	68	76
<i>n</i> -Butyl alcohol.....	116	71	57	64
Diethylcarbinol.....	116	71	48	97
<i>sec</i> -Amyl alcohol.....	119	76	61
Ethylene glycol monomethyl ether.....	125	113
1-Chloro-2-propanol.....	127	83
<i>sec</i> -Butylcarbinol.....	128	97	62
Ethylene chlorohydrin.....	129	101	51
Isoamyl alcohol.....	130	67	55	62
4-Methyl-2-pentanol.....	131	88	143	65
2-Chloro-1-propanol.....	132	76
Methylisobutylcarbinol.....	132	143
Ethylene glycol monoethyl ether.....	135	67
3-Hexanol.....	135	77
<i>n</i> -Amyl alcohol.....	138	68	46	46
Cyclopentanol.....	140	118	132
Triethylcarbinol.....	142
Acetoin.....	145
Hydroxyacetone (Acetol).....	146
2-Ethyl-1-butanol.....	149	51
2-Bromoethanol.....	150	86	76
Di- <i>n</i> -propylcarbinol.....	156	80	64
<i>n</i> -Hexyl alcohol.....	156	59	42	58
Cyclohexanol.....	160	128	82	112
2-Heptanol.....	160	54	49
Trimethylene chlorohydrin.....	161d.	76
2-Methylcyclohexanol.....	165	155	103
Furfuryl alcohol.....	170	129	45	80
Ethylene glycol mono- <i>n</i> -butyl ether.....	171
Pinacol.....	172
4-Methylcyclohexanol.....	174	160	125	130
3-Methylcyclohexanol.....	175	122	96
Diisobutylcarbinol.....	175	154?

TABLE XX—Continued
ALCOHOLS (LIQUIDS)—Continued

Name of Compound	B. P.	Derivatives		
		α -Naphthyl- urethan	Phenyl- urethan	3,5-Dinitro- benzoate
<i>n</i> -Heptyl alcohol.....	176°	62°	68°	47°
1,3-Dichloro-2-propanol.....	176	115	73
Trimethylene bromohydrin...	176d.	73
Tetrahydrofurfuryl alcohol.....	178	61	84
2-Octanol.....	179	63	114	32
Cyclohexylcarbinol.....	182
2,3-Dichloro-1-propanol.....	182	93	73
2-Ethyl-1-hexanol.....	184	61	34
Propylene glycol.....	188	153
Butyrolin.....	190
<i>n</i> -Octyl alcohol.....	192	66	74	61
Diethylene glycol mono- methyl ether.....	193
Ethylene glycol.....	197	176	157	169
Linalool.....	197	53	65
Diethylene glycol monoethyl ether.....	202
Methylphenylcarbinol.....	203	106	94	95
Benzyl alcohol.....	205	134	78	112
3-Chloro-1,2-propanediol.....	215d.
<i>n</i> -Nonyl alcohol.....	215	65	62	52
Trimethylene glycol.....	216	164	137	164
<i>m</i> -Tolylcarbinol.....	217	116
β -Phenylethyl alcohol.....	219	119	79	108
2,3-Dibromo-1-propanol.....	219	77	(α,β -Dibromo- mopropionic acid 64)
Ethylphenylcarbinol.....	219	102
1,3-Dibromo-2-propanol.....	219d.	84
Citronellol.....	222	(β -Methylad- ipic acid 89)
Geraniol.....	229	47	62
Diethylene glycol mono- <i>n</i> - butyl ether.....	231
<i>n</i> -Decyl alcohol.....	231	71	60	57
γ -Phenylpropyl alcohol.....	235	47	92
Diethylene glycol.....	245	149
Ethylene glycol monophenyl ether.....	245
Cinnamyl alcohol.....	250	114	90	121
Glycerol.....	290d.	191	180	(Tribenzoate 76)
Benzohydrol.....	297	136	140	141

TABLE XX—Continued

ALCOHOLS (SOLIDS)

Name of Compound	M. P.	α -Naphthyl-urethan	Phenyl-urethan	Miscellaneous
Acetoin.....	15°
Cyclohexanol.....	16	128°	82°	3,5-Dinitrobenzoate 112°
Trichloroethylalcohol.....	19
Lauryl alcohol.....	24	80	74	3,5-Dinitrobenzoate 60
Cinnamyl alcohol.....	33	114	90	3,5-Dinitrobenzoate 121
Pinacol.....	35	215	s-Tetramethyl-dichloroethane... 160
α -Terpineol.....	35	147	112	3,5-Dinitrobenzoate 78
o-Tolylcarbinol.....	36	79
Myristyl alcohol.....	39	71	4'-Iodobiphenylurethan..... 146
l-Menthol.....	42	128	111	Benzoate..... 55
Anisyl alcohol.....	45	94	Anisic acid..... 184
Pinacol hydrate.....	46
Cetyl alcohol.....	50	82	73	3,5-Dinitrobenzoate 66
Piperonyl alcohol.....	58	102
p-Tolylcarbinol.....	60
Benzohydrol.....	69	136	140	Benzoate..... 88
d-Sorbitol.....	98	Acetate..... 99
Terpinol.....	102	Hydrochloride..... 50
Terpinol hydrate.....	117	Hydrochloride..... 50
Benzoin.....	133	140	165	(See ketones)
Sitosterol.....	137	Acetate..... 127
l-Cholesterol.....	148	160	168	Benzoate..... 150
Triphenylcarbinol.....	162	Triphenylmethane... 92
Ergosterol.....	165	Acetate..... 180
d-Mannitol.....	166	303	Hexaacetate..... 120
Benzopinacol.....	186
d-Borneol.....	208	132	138	p-Nitrobenzoate... 137
Inositol.....	225	Hexaacetate..... 216
Pentaerythritol.....	253	Tetraacetate..... 84

TABLE XXI
ALDEHYDES (LIQUIDS)

Name of Compound	B. P.	Derivatives			
		Oxime	Semi-carba- zone	Phenyl- hydra- zone	2,4-Dini- trophenyl- hydra- zone
Formaldehyde.....	-21°	169°	166°
Acetaldehyde.....	21	47°	162	{ 63° 99 }	{ 147 168 }
Propionaldehyde.....	50	40	{ 89 154 }	154
Glyoxal.....	50	178	270	180	328
Acrolein.....	52	171	52 *	165
Isobutyraldehyde.....	64	125	182
α -Methylacrolein.....	73	198	74 *	206
<i>n</i> -Butyraldehyde.....	74	104	122
Isovaleraldehyde.....	92	48	107	123
Chloral.....	98	56	131
<i>n</i> -Valeraldehyde.....	103	52	106
Crotonaldehyde.....	103	119	199	56	190
α -Ethyl- <i>n</i> -butyraldehyde.....	116	96	134
Paraldehyde.....	124
<i>n</i> -Caproaldehyde.....	128	51	106	104
<i>n</i> -Heptaldehyde.....	156	57	109	108
Furfural.....	161	{ 89 74 }	202	97	229
α -Ethyl- <i>n</i> -caproaldehyde.....	163	254d.	121
Bromal.....	174	115
Benzaldehyde.....	179	35	222	158	237
5-Methylfurfural.....	187	{ <i>syn</i> 112 <i>anti</i> 52 }	211	148	212
Phenylacetaldehyde.....	194	103	156	58	121
Salicylaldehyde.....	196	57	231	142	252d.
<i>m</i> -Tolualdehyde.....	199	60	204	84	194
<i>o</i> -Tolualdehyde.....	200	49	212	101	193
<i>p</i> -Tolualdehyde.....	204	{ 79 110 }	234	114	234
Citronellal.....	206	82	77
<i>o</i> -Chlorobenzaldehyde.....	208	75	225	86	207
<i>m</i> -Chlorobenzaldehyde.....	208	70	228	134
Hydrocinnamaldehyde.....	224	94	127	149
Citral.....	228d.	164	116

* Pyrazosine.

TABLE XXI—Continued

ALDEHYDES (LIQUIDS)

Name of Compound	B. P.	Derivatives			
		Oxime	Semi-carba-zone	Phenyl-hydra-zone	2,4-Dinitrophenyl-hydra-zone
<i>m</i> -Bromobenzaldehyde...	236°	72°
Anisaldehyde (<i>p</i> -Methoxybenzaldehyde).....	247	$\left\{ \begin{array}{l} \alpha-45 \\ \alpha'-64 \\ \beta-133 \end{array} \right\}$	210°	120°	254°d.
Cinnamaldehyde.....	252	138	215	168	255d.
Veratric aldehyde.....	285	95	177	121	265

ALDEHYDES (SOLIDS)

Name of Compound	M. P.	B. P.	Derivatives			
			Oxime	Semi-carba-zone	Phenyl-hydra-zone	2,4-Dinitrophenyl-hydra-zone
Piperonal.....	37°	263°	110°	230°	100°	266°d.
<i>o</i> -Nitrobenzaldehyde...	44	102	255	156	250d.
<i>p</i> -Chlorobenzaldehyde...	47	214	106	230	127
Phthalaldehyde.....	56	191
<i>m</i> -Nitrobenzaldehyde...	58	120	246	124	293d.
Veratric aldehyde.....	58	285	95	177	121	265
β -Naphthaldehyde.....	60	156	245	206d.	270
<i>p</i> -Bromobenzaldehyde...	67	$\left\{ \begin{array}{l} \text{syn } 157 \\ \text{anti } 111 \end{array} \right\}$	228	113
2,4-Dichlorobenzaldehyde.....	71	136
Vanillin.....	80	285d.	117	229	105	271d.
Phenylglyoxal.....	$\left\{ \begin{array}{l} \text{hydrate} \\ 91 \end{array} \right\}$	$\left\{ \begin{array}{l} \alpha-129 \\ \text{di-168} \end{array} \right\}$	$\alpha-217d.$	di-152
<i>m</i> -Hydroxybenzaldehyde.....	105	131	260d.
<i>p</i> -Nitrobenzaldehyde...	106	129	221	159	320
Metalddehyde.....	115
<i>p</i> -Hydroxybenzaldehyde.....	115	72	224	177	280d.
Terephthalaldehyde...	116	245	200	$\left\{ \begin{array}{l} 154 \\ 278 \end{array} \right\}$
<i>dl</i> -Glyceraldehyde.....	142	167
Protocatechualdehyde.	154	157	175	275

TABLE XXII
AMIDES (LIQUIDS)

Name of Compound	B. P.	Name of Compound	B. P.
<i>N,N</i> -Diethylformamide.....	176°	Formylpiperidine.....	222°
Formamide.....	195d.	Acetyl piperidine.....	226

AMIDES (SOLIDS)

Name of Compound	M. P.	Name of Compound	M. P.
Formanilide.....	46°	Semicarbazide.....	96°
Benzoylpiperidine.....	48	Stearanilide.....	97
Ethyl carbamate.....	49	<i>p</i> -Acetoxy- <i>N</i> -methylacetanilide.....	98
<i>N-n</i> -Propylacetanilide.....	50	α,α -Dichloroacetamide.....	98
Methyl carbamate.....	52	<i>N,N</i> -Diphenylacetamide.....	101
<i>n</i> -Butyl carbamate.....	54	Methylurea.....	101
<i>N</i> -Ethylacetanilide.....	54	<i>n</i> -Caproamide.....	101
Isobutyl carbamate.....	55	<i>N</i> -Methylacetanilide.....	102
<i>N</i> -Methyl- <i>o</i> -acetotoluide.....	56	Propionanilide.....	103
<i>n</i> -Propyl carbamate.....	60	Palmitamide.....	106
Ethyl hippurate.....	60	Chaulmoogramide.....	106
Isoamyl carbamate.....	64	Isovaleranilide.....	109
<i>m</i> -Acetotoluide.....	65	Hydrobenzamide.....	110
Ethyl oxanilate.....	66	<i>o</i> -Acetotoluide.....	112
<i>N,N</i> -Diphenylformamide.....	73	Acetanilide.....	114
Propionamide.....	79	Ethyl oxamate.....	114
α,β -Diethylcarbanilide.....	79	<i>n</i> -Butyramide.....	115
Allylurea.....	80	2-Brom- <i>o</i> -4-methylacetanilide.....	117
Acetamide.....	82	α -Phenylacetanilide.....	117
<i>N</i> -Methyl- <i>p</i> -acetotoluide.....	83	<i>N</i> -Ethyl- <i>p</i> -nitroacetanilide.....	118
Acetoacetanilide.....	85	α -Chloroacetamide.....	119
<i>o</i> -Chloroacetanilide.....	88	α,β -Dimethylcarbanilide.....	121
<i>n</i> -Butyl oxamate.....	88	Succinimide.....	125
Isopropyl carbamate.....	92	<i>n</i> -Butylethylbarbituric acid.....	125
<i>o</i> -Nitroacetanilide.....	92	Ethyl- <i>n</i> -hexylbarbituric acid.....	126
<i>n</i> -Heptamide.....	94	<i>p</i> -Methoxyacetanilide.....	127
4-Methyl-2-nitroacetanilide.....	94	α -Acetyl- β -phenylhydrazine.....	128
<i>N</i> -Methyl- <i>N</i> - α -naphthylacetamide.....	95		
<i>n</i> -Butyranilide.....	95		

TABLE XXII—*Continued*AMIDES (SOLIDS)—*Continued*

Name of Compound	M. P.	Name of Compound	M. P.
Benzamide.....	128°	<i>p</i> -Hydroxyacetanilide.....	169°
Isobutyramide.....	128	Alloxan.....	170d.
Piperine.....	129	Malonamide.....	170
Urea (Carbamide).....	132	Ethylphenylbarbituric acid..	172
2,4-Dimethylacetanilide.....	133	Diallylbarbituric acid.....	172
<i>N</i> - β -Naphthylacetamide.....	134	<i>p</i> -Phenetylurea.....	174
Phenacetin.....	135	<i>o</i> -Nitrobenzamide.....	176
Salicylamide.....	139	<i>p</i> -Chloroacetanilide.....	179
α,α,α -Trichloroacetamide.....	140	α -Acetyl- β -methylurea.....	180
<i>o</i> -Toluamide.....	140	<i>p</i> -Tolylurea.....	181
<i>m</i> -Tolylurea.....	142	<i>p</i> -Iodoacetanilide.....	182
Furamide.....	142	Thiourea.....	182
Cinnamamide.....	142	3,5-Dinitrobenzamide.....	183
<i>o</i> -Benzotoluide.....	142	<i>o</i> -Iodobenzamide.....	183
<i>m</i> -Nitrobenzamide.....	143	<i>N,N'</i> -Diacetyl- <i>o</i> -phenylene-	
α -Triphenylguanidine.....	145	diamine.....	185
α -Bromoisovalerylurea.....	145	<i>m</i> -Iodobenzamide.....	186
Phenylurea.....	147	Hippuric acid.....	187
Diphenylguanidine.....	147	Diethylbarbituric acid.....	188
4-Methyl-3-nitroacetanilide..	148	<i>p</i> -Bromobenzamide.....	189
Benzylurea.....	149	<i>as</i> -Diphenylurea.....	189
Nitrourea.....	150d.	<i>N,N'</i> -Diacetyl- <i>m</i> -phenylene-	
<i>p</i> -Acetotoluide.....	153	diamine.....	191
<i>N</i> -Methyl- <i>p</i> -nitroacetanilide.	153	<i>o</i> -Tolylurea.....	192
<i>m</i> -Nitrobenzanilide.....	153	Biuret.....	192d.
Cinnamanilide.....	153	2-Methyl-4-nitroacetanilide..	196
Ethylisoamylbarbituric		Isatin.....	200
acid.....	154	<i>p</i> -Nitrobenzamide.....	201
α -Phenylacetamide.....	154	Ethylisopropylbarbituric	
<i>o</i> -Bromobenzamide.....	155	acid.....	201
<i>m</i> -Bromobenzamide.....	155	<i>N</i> -Phenylphthalimide.....	205
<i>m</i> -Nitroacetanilide.....	155	Dicyanodiamide.....	207
<i>N</i> -Phenylsuccinimide.....	156	<i>p</i> -Nitroacetanilide.....	210
<i>p</i> -Benzotoluide.....	158	<i>p</i> -Iodobenzamide.....	217
<i>N</i> - α -Naphthylacetamide.....	159	Acetylurea.....	218
<i>p</i> -Toluamide.....	160	<i>s</i> -Di- <i>m</i> -tolylurea.....	218
Benzanilide.....	161	Hydantoin.....	218
<i>N</i> - α -Naphthylbenzamide.....	161	Phthalamide.....	219d.
<i>p</i> -Aminoacetanilide.....	162	Saccharin.....	220
<i>p</i> -Bromoacetanilide.....	167	Succinanilide.....	226
α -Benzoyl- β -phenylhydra-		Nitroguanidine.....	230d.
zine.....	168	Phthalamide.....	233

TABLE XXII—*Continued*AMIDES (SOLIDS)—*Continued*

Name of Compound	M. P.	Name of Compound	M. P.
Caffeine.....	234°	Creatinine.....	292°d.
Carbanilide(<i>s</i> -Diphenylurea) .	238	<i>N,N'</i> -Diacetyl- <i>p</i> -phenylene- diamine.....	300
<i>p</i> -Hydroxy- <i>N</i> -methylacetan- ilide.....	240	Creatine.....	315d.
Barbituric acid.....	245	Theobromine.....	337
Succinamide.....	250		subl.
<i>s</i> -Di- <i>o</i> -tolylurea.....	250	Xanthine.....	360
Oxanilide.....	257	Oxamide.....	419d.
Theophylline.....	264	Uric acid.....	d.
<i>s</i> -Di- <i>p</i> -tolylurea.....	268		

TABLE XXIII
 AMINES—PRIMARY AND SECONDARY (LIQUIDS)

Name of Compound	B. P.	Benzene-sulfonamide	Benzamide	<i>p</i> -Toluenesulfonamide	Phenylthiourea
Methylamine.....	-6°	30°	80°	75°	113°
Dimethylamine.....	7	47	41	79	135
Ethylamine.....	19	58	71	63	106
Isopropylamine.....	33	26	101
<i>N</i> -Methylethylamine.....	35
<i>n</i> -Propylamine.....	49	36	84	52	63
Diethylamine.....	55	42	42	60	34
Allylamine.....	56	39	64	98
<i>sec</i> -Butylamine.....	63	70	76	55	101
Isobutylamine.....	69	53	57	78	82
<i>n</i> -Butylamine.....	77	65
Diisopropylamine.....	86
Pyrrolidine.....	89	123
Isoamylamine.....	95	102
<i>n</i> -Amylamine.....	104	69
Piperidine.....	105	93	48	96	101

AMINES—PRIMARY AND SECONDARY (LIQUIDS)

Name of Compound	B. P.	Benzene-sulfonamide	Acetamide	Benzamide	<i>p</i> -Toluenesulfonamide	Phenylthiourea
Di- <i>n</i> -propylamine.....	110°	51°	69°
Diallylamine.....	111
Ethylenediamine.....	116	168	172°	249°	160°	102
1,2-Diaminopropane.....	120	139	192	103
<i>n</i> -Hexylamine.....	128	96	40	77
Morpholine.....	130	118	75	147	136
Cyclohexylamine.....	134	89	104	149	148
2-Amino-4-chlorophenol.....	134	183
1,3-Diaminopropane.....	136	96	126	147	148
Diisobutylamine.....	139	55	86	113
<i>n</i> -Heptylamine.....	155	75
Di- <i>n</i> -butylamine.....	160	86
1,4-Diaminobutane.....	160	168
2-Hydroxyethylamine.....	171
1,5-Diaminopentane.....	178	119	148
<i>n</i> -Octylamine.....	180
Aniline.....	183	112	114	160	103	154
Benzylamine.....	184	88	60	105	116	156
<i>N</i> -Methylbenzylamine.....	185	95

TABLE XXIII—*Continued*
 AMINES—PRIMARY AND SECONDARY (LIQUIDS)—*Continued*

Name of Compound	B. P.	Benzene-sulfonamide	Acetamide	Benzamide	<i>p</i> -Toluenesulfonamide	Phenylthiourea
α -Phenylethylamine.....	185°	120°
Diisobutylamine.....	187	72°
Methylaniline.....	192	79°	102°	63	94°	87
β -Phenylethylamine.....	198	69	114	116	135
<i>o</i> -Toluidine.....	199	124	112	143	108	136
<i>N</i> -Ethylbenzylamine.....	199	50
<i>m</i> -Toluidine.....	203	95	65	125	114	94
<i>N</i> -Ethylaniline.....	205	54	60	87	89
Di- <i>n</i> -amylamine.....	205	72
<i>l</i> -Menthylamine.....	205	145	156	135
<i>N</i> -Methyl- <i>m</i> -toluidine.....	206	66
<i>o</i> -Chloroaniline.....	207	129	87	99	105	156
<i>N</i> -Methyl- <i>o</i> -toluidine.....	207	55	66	120
<i>N</i> -Methyl- <i>p</i> -toluidine.....	208	64	83	53	60	89
4-Amino-1,3-dimethylbenzene.....	212	128	133	192	133
<i>N</i> -Isopropylaniline.....	213	39
<i>N</i> -Methyl- <i>o</i> -chloroaniline..	214
2-Amino-1,4-dimethylbenzene.....	215	138	139	140	119
<i>m</i> -Ethylaniline.....	215
2-Amino-1,3-dimethylbenzene.....	216	176	168	204
<i>o</i> -Ethylaniline.....	216	111	147
<i>p</i> -Ethylaniline.....	216	94	151	104
<i>N</i> -Ethyl- <i>p</i> -toluidine.....	217	66	40	70
<i>o</i> -Amino- <i>N,N</i> -dimethylaniline.....	217
<i>N</i> -Ethyl- <i>o</i> -toluidine.....	218	62	72	75
5-Amino-1,3-dimethylbenzene.....	220	144
<i>N</i> -Ethyl- <i>m</i> -toluidine.....	221	72
4- <i>N</i> -Methylamino-1,3-dimethylbenzene.....	221
<i>N-n</i> -Propylaniline.....	222	54	47	56	104
3-Chloro-4-aminotoluene...	223	113	137
<i>o</i> -Anisidine.....	225	89	84	60	127	136
Cumidine.....	225	102	162
α -Methyl- α -phenylhydrazine.....	227	132	92	153
Mesidine.....	229	137	216	204	193

TABLE XXIII—*Continued*AMINES—PRIMARY AND SECONDARY (LIQUIDS)—*Continued*

Name of Compound	B. P.	Benzene-sulfonamide	Acetamide	Benzamide	<i>p</i> -Toluenesulfonamide	Phenylthiourea
<i>o</i> -Phenetidine.....	229°	102°	79°	104°	137°
<i>m</i> -Chloroaniline.....	230	121	72	120	124
<i>N</i> -Isobutylaniline.....	231
<i>N-n</i> -Butylaniline.....	236
4-Amino-3-bromotoluene.....	240	117	149	154
<i>N</i> -Methyl- <i>p</i> -chloroaniline.....	240	92
5-Chloro-2-aminotoluene.....	241	140
2-Amino-4-isopropyl-toluene.....	242	71	102
Phenylhydrazine.....	243	148	128	168	151°	172
<i>o</i> -Amino- <i>N</i> -methylaniline.....	245
<i>m</i> -Phenetidine.....	248	97	103	157	138
Tetrahydroquinoline.....	250	67	75
<i>o</i> -Bromoaniline.....	250	99	116	146
<i>m</i> -Anisidine.....	251	81	68
<i>m</i> -Bromoaniline.....	251	87	136	97
<i>N</i> -Isoamylaniline.....	254
<i>p</i> -Phenetidine.....	254	143	135	173	106	136
Isoduridine.....	255	211
<i>p</i> -Amino- <i>N</i> -methylaniline.....	258	165
<i>N</i> -Methyl- <i>p</i> -bromoaniline.....	260
Methyl anthranilate.....	260d.	107	101	100
<i>p</i> -Amino- <i>N,N</i> -diethylaniline.....	262
Ethyl anthranilate.....	265d.	92	61	98
Di-(2-hydroxyethyl)-amine (Diethanolamine).....	268
<i>ar</i> -Tetrahydro- α -naphthylamine.....	275	158
<i>ar</i> -Tetrahydro- β -naphthylamine.....	275	107
<i>N</i> -Methyl- α -naphthylamine.....	293	95	121
Ethyl <i>m</i> -aminobenzoate.....	294	110	148
<i>N</i> -Benzylaniline.....	298	119	58	107	103
Dibenzylamine.....	300	68	112
Diphenylamine.....	302	124	101	180	144	152
<i>N</i> -Methyl- β -naphthylamine.....	309	107
<i>N</i> -Ethyl- β -naphthylamine.....	315	49
<i>N</i> -Ethyl- α -naphthylamine.....	325	68

TABLE XXIII—Continued

AMINES—PRIMARY AND SECONDARY (SOLIDS)

Name of Compound	M. P.	B. P.	Benzesul- fonamide	Acetyl Derivative	Benzamide	<i>p</i> -Toluenesul- fonamide	Phenylthio- urea
Ethyl anthranilate.....	13°	265°d.	92°	61°	98°
2-Amino-1,4-dimethylben- zene.....	15	215	138	139	140	119°
<i>m</i> -Bromoaniline.....	18	251	87	136	97°
Phenylhydrazine.....	19	243	148	128	168	151	172
Tetrahydroquinoline.....	20	250	67	75
Methyl anthranilate.....	24	260d.	107	101	100
Isoduridine.....	24	255	211
4-Amino-3-bromotoluene.....	26	240	117	149	154
<i>m</i> -Iodoaniline.....	27	119	157	128
Di-(2-hydroxyethyl)amine (Diethanolamine).....	28	268
5-Chloro-2-aminotoluene.....	29	241	140
<i>o</i> -Bromoaniline.....	31	250	99	116	161
<i>as</i> -Diphenylhydrazine.....	34	184	192
<i>N</i> -Benzylaniline.....	37	298	119	58	107	103
<i>ar</i> -Tetrahydro- β -naph- thylamine.....	38	275	107
<i>N</i> -Methyltribromoaniline.....	39	101
5-Chloro-4-amino-1,2-di- methylbenzene.....	40	148
<i>p</i> -Amino- <i>N,N</i> -dimethyl- aniline.....	41	262	130	228
<i>N</i> -Methylpseudocumidine.....	44	237
4-(<i>N</i> -Methylamino)-2- nitrotoluene.....	45	128
2,4'-Diaminobiphenyl.....	45	363	202	278
<i>p</i> -Toluidine.....	45	200	120	153	158	117	141
2-Aminobiphenyl.....	45	299	119	86
4-Amino-1,2-dimethylben- zene.....	49	226	118	99	154
2,5-Dichloroaniline.....	50	251	132	120
α -Naphthylamine.....	50	300	167	159	160	157	165
2-Amino-3,5-dichloroto- luene.....	50	186
Indole.....	52	254	68
4-Aminobiphenyl.....	53	302	171	230
Diphenylamine.....	54	302	124	101	180	141	152
2-Aminopyridine.....	56	165

TABLE XXIII—Continued

AMINES—PRIMARY AND SECONDARY (SOLIDS)—Continued

Name of Compound	M. P.	B. P.	Benzenesul- fonamide	Acetyl Derivative	Benzamide	<i>p</i> -Toluenesul- fonamide	Phenylthio- urea
<i>o</i> -Iodoaniline.....	56°	109°
<i>n</i> -Butyl <i>p</i> -aminobenzoate.....	56
<i>p</i> -Anisidine.....	57	243°	95°	127	154°	114°	171
4-(<i>N</i> -Ethylamino)-3-nitro- toluene.....	59	127
2-Amino-5-bromotoluene.....	59	156
4-Amino-3,5-dichloro- toluene.....	60
2,3-Diaminotoluene.....	61	255
<i>N</i> -Phenyl- α -naphthyl- amine.....	62	335	115	152
<i>p</i> -Iodoaniline.....	62	183	222	153
<i>m</i> -Phenylenediamine.....	63	283	194	191	240	172
<i>p</i> -Amino- <i>N</i> -methylacetan- ilide.....	63
2,4-Dichloroaniline.....	63	245	128	145	117	126
2,5-Diaminotoluene.....	64	120
<i>m</i> -Nitro- <i>N</i> -ethylaniline.....	65	89
<i>p</i> -Tolylhydrazine.....	65	121	146
<i>p</i> -Bromoaniline.....	66	245d.	134	167	204	148
<i>N</i> -Methyl- <i>m</i> -nitroaniline.....	66	83	95	156
1,8-Diaminonaphthalene.....	67
Pseudocumidine.....	68	235	136	161	167
<i>p</i> -Chloroaniline.....	70	232	121	179	192	95	152
<i>o</i> -Nitroaniline.....	71	104	92	94	142
4-Methyl-3-nitroaniline.....	72	160	93	172
2-Chloro-3,5-diamino- toluene.....	73	228
4-Nitromesidine.....	75	163	191	169
4-Aminodiphenylamine (anhydrous).....	75	158	203
4-Amino-5-nitro-1,3- dimethylbenzene.....	76	173	185
4-Amino-2-nitrotoluene.....	77	160	148	172	164	171
2,4,6-Trichloroaniline.....	77	262	204	174
3,5-Dibromo-4-aminotolu- ene.....	78	183

TABLE XXIII—Continued

AMINES—PRIMARY AND SECONDARY (SOLIDS)—Continued

Name of Compound	M. P.	B. P.	Benzenesul- fonamide	Acetyl Derivative	Benzamide	<i>p</i> -Toluenesul- fonamide	Phenylthio- urea
<i>N</i> - <i>p</i> -Tolyl- α - naphthylamine.....	79°	83°	124°	140°
2,4-Dibromoaniline.....	79	146	134	134°
Di- <i>p</i> -tolylamine.....	79	330°	85	125
2,4-Diaminophenol.....	79d.
2-Aminodiphenylamine...	80
3-Amino-6-chlorotoluene...	83	241	91
2,6-Dibromoaniline.....	83	210
4-(<i>N</i> -Methylamino)-3- nitrotoluene.....	84	64
<i>p</i> -Hydroxy- <i>N</i> -methyl- aniline.....	85	$\left\{ \begin{array}{l} 240 \\ \text{(mono)} \\ 97 \\ \text{(di)} \end{array} \right\}$	175
<i>o</i> -Hydroxy- <i>N</i> -methylani- line.....	87	150	150
2,4-Diaminobenzene.....	88	$\left\{ \begin{array}{l} 170 \\ \text{(mono)} \\ 243 \\ \text{(di)} \end{array} \right\}$	178	$\left\{ \begin{array}{l} 215 \\ \text{(di)} \end{array} \right\}$
Ethyl <i>p</i> -aminobenzoate...	89	110	148
3,4-Diaminotoluene.....	89	265
2-Methyl-6-nitroaniline...	91	157	167
<i>p,p'</i> -Diaminodiphenylme- thane.....	94	228
2-Methyl-3-nitroaniline...	95	158
6-Chloro-2,4-dibromoani- line.....	95	227	192
1,2-Diaminonaphthalene...	95	234	291
2,4-Diiodoaniline.....	96	181
<i>N</i> -Ethyl- <i>p</i> -nitroaniline...	96	118	98	107
Semicarbazide.....	96	165	225
2-Amino-3-nitrotoluene...	97	158
8-Nitro-1-naphthylamine...	97	194	191
4-Chloro-1-naphthylamine	98	184
2,4-Diaminotoluene.....	99	280	178	224	224	192
<i>o</i> -Phenylenediamine.....	102	256	185	185	301	201
<i>p</i> -Tolyl- β -naphthylamine.	103	85	139

TABLE XXIII—*Continued*AMINES—PRIMARY AND SECONDARY (SOLIDS)—*Continued*

Name of Compound	M. P.	B. P.	Benzenesul- fonamide	Acetyl Derivative	Benzamide	<i>p</i> -Toluenesul- fonamide	Phenylthio- urea
Piperazine.....	104°	140°	282°	134°	191°
<i>p</i> -Aminoacetophenone....	106	295	128	167	205	203°
<i>p</i> -Bromophenylhydrazine....	106
2-Amino-4-nitrotoluene....	107	172	150
<i>N</i> -Phenyl- β -naphthyl- amine.....	108	93	148
β -Naphthylamine.....	112	300	102	132	162	133	129°
<i>N</i> -Ethyl-2,4-dinitroaniline	113
<i>m</i> -Nitroaniline.....	114	284	136	155	155	138	160
4-Amino-3-nitrotoluene....	116	102	96	148	166
2,4,6-Tribromoaniline....	119	300	127 (di) 232 (mono)	198
5-Nitro-1-naphthylamine....	119	183	220
1,4-Diaminonaphthalene...	120	303	280
<i>m</i> -Aminophenol.....	122	101 (di) 148 (mono)	153	157	156
4-Amino-6-nitro-1,3- dimethylbenzene.....	123	149	159	200
<i>p</i> -Aminobenzophenone....	124	153	152
<i>p</i> -Aminoazobenzene.....	125	360	144
1-Nitro-2-naphthylamine....	126	156	124	159
Benzidine.....	127	400	232	317	352	243
<i>o</i> -Tolidine.....	129	314	265
2-Amino-5-nitrotoluene....	130	158	198	174
3-Amino-6-nitrotoluene....	135	102
Bianisidine.....	135	242	236
2,6-Dinitroaniline.....	138	197
<i>p</i> -Phenylenediamine.....	140	267	247	304	300	266
2-Amino-5-nitro-1,4- dimethylbenzene.....	142	162	166
2-Amino-5-nitronaphtha- lene.....	144	186	182

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TABLE XXIII—Continued

AMINES—PRIMARY AND SECONDARY (SOLIDS)—Continued

Name of Compound	M. P.	B. P.	Benzenesul- fonamide	Acetyl Derivative	Benzamide	<i>p</i> -Toluenesul- fonamide	Phenylthio- urea
1-Amino-2-nitronaphtha- lene.....	144°	199°	175°
<i>p</i> -Nitroaniline.....	147	139°	215	199	191°
<i>p</i> -Nitro- <i>N</i> -methylaniline..	152	120	153	111
<i>p</i> -Nitrophenylhydrazine..	157d.	205	193
<i>p</i> -Aminoacetanilide.....	162	304
4-Amino-3,5-dinitrotolu- ene.....	166
Picramic acid.....	168	201	220
4-Amino-2,6-dinitro- toluene.....	169
5-Amino-2-hydroxytoluene	173	$\left\{ \begin{array}{l} 103 \\ \text{(di)} \\ 179 \\ \text{(mono)} \end{array} \right\}$	194
<i>o</i> -Aminophenol.....	174	141	201	182	139	146°
<i>N</i> -Methyl-2,4-dinitro- aniline.....	176
2,4-Dinitroaniline.....	180	120	202	219
<i>p</i> -Aminophenol.....	184d.	125	$\left\{ \begin{array}{l} 150 \\ \text{(di)} \\ 168 \\ \text{(mono)} \end{array} \right\}$	234	150
2,4,6-Trinitroaniline (Picramide).....	190	211	230
Dinitromesidine.....	194	275
1-Amino-4-nitronaphtha- lene.....	195	153	190	224	185
2,4-Dinitrophenylhydra- zine.....	198d.	197	206
4,4'-Diaminostilbene.....	226	312
Carbazole.....	243	351°	69	98
<i>m</i> -Aminoacetanilide.....	279	191
2-Aminoanthraquinone....	302	271	257	228	304

TABLE XXIV

AMINES—TERTIARY (LIQUIDS)

Name of Compound	B. P.	Addition Compounds with			
		Chloro- platinic Acid	Methyl <i>p</i> -Tol- uene- sulfonate	Methyl Iodide	Pic- ric Acid
Trimethylamine.....	3°	242°d.	230°d.	216°
Triethylamine.....	89	173
Pyridine.....	116	241	139°	117	167
α -Picoline.....	129	195d.	150	230	169
β -Dimethylaminoethyl alco- hol.....	133	96
Tri- <i>n</i> -propylamine.....	153	116
Triallylamine.....	155
2,4-Lutidine.....	159	113	180
β -Diethylaminoethyl alcohol	161
<i>d</i> -Coniine.....	170	{ 78 (hy- drated) 175 (an- hydrous) }	75
2,4,6-Collidine.....	172	155
<i>N,N</i> -Dimethyl- <i>o</i> -toluidine...	185	193d.	122
<i>N,N</i> -Dimethylbenzylamine...	185	192	179
Dimethylaniline.....	193	173d.	161	228d.	163
<i>N</i> -Ethyl- <i>N</i> -methylaniline...	201	125	134
<i>N,N</i> -Diethyl- <i>o</i> -toluidine...	206	224d.	180
<i>N,N</i> -Dimethyl- <i>o</i> -chloroanil- ine.....	207
<i>N,N</i> -Dimethyl- <i>p</i> -toluidine...	210	85	219	127
Tri- <i>n</i> -butylamine.....	211	180	105
<i>N,N</i> -Dimethyl- <i>m</i> -toluidine...	212	177
<i>N,N</i> -Dimethylmesidine.....	213
<i>N,N</i> -Diethylaniline.....	218	102	142
<i>N,N</i> -Dimethylpseudocumi- dine.....	220
<i>N,N</i> -Diethyl- <i>p</i> -toluidine...	229	172
<i>N,N</i> -Dimethyl- <i>p</i> -chloroani- line.....	230
<i>N,N</i> -Diethyl- <i>m</i> -toluidine...	231	97

TABLE XXIV—Continued

AMINES—TERTIARY (LIQUIDS)—Continued

Name of Compound	B. P.	Addition Compounds with			
		Chloro- platinic Acid	Methyl <i>p</i> -Tol- uene- sulfonate	Methyl Iodide	Pic- ric Acid
Quinoline.....	239°	218°	126°	{ 72° (hy- drated) 133 (an- hyd.) }	203°
Isoquinoline.....	240	263d.	163	159°	222
<i>dl</i> -Nicotine.....	242	218
<i>N,N</i> -Di- <i>n</i> -propylaniline...	245	156
Triisoamylamine.....	245	125
Quinaldine.....	247	226	161	195	191
Tri- <i>n</i> -amylamine.....	257	80d.
6-Methylquinoline.....	258	154	219	229
<i>N,N</i> -Di- <i>n</i> -butylaniline.....	261	180	125
Lepidine(4-Methylquinoline)	263
<i>N,N</i> -Dimethyl- <i>p</i> -bromo- aniline.....	265
2-Phenylpyridine.....	269
<i>N,N</i> -Dimethyl- α -naphthyl- amine.....	272
<i>N</i> -Methyldiphenylamine...	296
<i>N,N</i> -Dimethyl-2,4,6-tribro- moaniline.....	301
<i>N,N</i> -Dimethyl- β -naphthyl- amine.....	305
6-Methoxyquinoline.....	305d.
<i>N</i> -Benzyl- <i>N</i> -methylaniline.	306	164	103
<i>N</i> -Benzyl- <i>N</i> -ethylaniline...	312d.	161	117

TABLE XXIV—*Continued*
 AMINES—TERTIARY (SOLIDS)

Name of Compound	M. P.	B. P.	Addition Compounds with		
			Methyl <i>p</i> -Toluene- sulfonate	Methyl Iodide	Picric Acid
Isoquinoline.....	24°	240°	163°	159°	222°
6-Methoxyquinoline.....	28	305d.
<i>p</i> -Bromo- <i>N,N</i> -diethylaniline	34	270
<i>p</i> -Bromo- <i>o,N,N</i> -dimethyl- aniline.....	55	264	185
2,6-Dimethylquinoline.....	60	265	175	237	178
<i>m</i> -Nitro- <i>N,N</i> -dimethyl- aniline.....	60	285	205
<i>N</i> -Phenylpyrrole.....	61	234
<i>N,N</i> -Dibenzylaniline.....	70	300d.	135	131d.
<i>p</i> -Dimethylaminobenzal- dehyde.....	73
8-Hydroxyquinoline.....	75	266	143d.	204
<i>p</i> -Hydroxy- <i>N,N</i> -dimethyl- aniline.....	76	201
<i>N,N</i> -Diethyl-2,4-dinitroanil- ine.....	80
<i>p</i> -Nitroso- <i>N,N</i> -diethylanil- ine.....	84
<i>m</i> -Hydroxy- <i>N,N</i> -dimethyl- aniline.....	85	268	182
<i>p</i> -Nitroso- <i>N,N</i> -dimethyl- aniline.....	87	140
<i>N,N</i> -Dimethyl-2,4-dinitro- aniline.....	87
Tribenzylamine.....	91	380	184	190
Acridine.....	108	224	208
Antipyrine.....	113
<i>p</i> -Dimethylaminoazoben- zene.....	117	174
Triphenylamine.....	127
Methyleneaminoacetonitrile	129
6-Nitroquinoline.....	149
<i>p</i> -Nitro- <i>N,N</i> -dimethylani- line.....	163
6-Nitroquinaldine.....	164
<i>p,p'</i> -Bis(dimethylamino)- benzophenone.....	174	105	156
2-Hydroxyquinoline.....	199
Hexamethylenetetramine...	280	205	190

TABLE XXV

AMINO ACIDS*

Name of Compound	Decomposition Point	Derivatives			
		Benzoyl	Phenyl-urea	p-Toluenesulfonyl	Miscellaneous
<i>N</i> -Phenylglycine . . .	126°	63°	195°
Anthranilic acid. . . .	144	182	181	Acetyl. . . . 185°
<i>dl</i> -Hydroxyglutamic acid.	150
<i>m</i> -Aminobenzoic acid	174	248	270	Acetyl. . . . 250
<i>p</i> -Aminobenzoic acid. .	186	278	300	Acetyl. . . . 252
β -Alanine.	196	174
<i>d</i> - or <i>l</i> -Glutamic acid. .	198	138	117°	α -Naphthyl-urea. . . . 236
<i>p</i> -Aminophenylacetic acid.	200	198	Acetyl. . . . 170
<i>dl</i> -Proline.	203	170	Picrate. . . . 137
Sarcosine.	210	102	Acetyl. . . . 135
<i>l</i> -Proline.	222	170	133	Picrate. . . . 154
<i>d</i> - or <i>l</i> -Lysine.	224	184	Dibenzoyl. . 145
<i>d</i> - or <i>l</i> -Asparagine. . .	226	164	Picrate. . . . 180d.
<i>dl</i> -Glutamic acid. . . .	227	157
<i>dl</i> -Serine.	228	171	169	213	β -Naphthalenesulfonyl. 220
Glycine.	232	187	163	147	Acetyl. . . . 206
<i>dl</i> -Threonine.	235	148 (mono)
<i>d</i> -Arginine.	238	Picrate. . . . 206
<i>dl</i> -Arginine.	238	315	Picrate. . . . 201
<i>p</i> -Hydroxyphenylglycine.	248	117	Acetyl. . . . 203
<i>dl</i> -Allothreonine. . . .	252	177
<i>d</i> - or <i>l</i> -Threonine. . . .	253	148 (mono)
<i>l</i> -Cystine.	260	181	117	203d.
<i>l</i> -Glycylglycine.	264	176
<i>d</i> - or <i>l</i> -Aspartic acid. .	270	185	162	140	α -Naphthyl-urea. . . . 115
<i>l</i> -Hydroxyproline. . . .	270	175	153
<i>d</i> - or <i>l</i> -Allothreonine. .	272	128
<i>dl</i> -Methionine.	272	151	Acetyl. . . . 114
Creatinine.	292	Picrate. . . . 220

* An italicized letter (*d* or *l*), when placed before the name of an amino acid, indicates rotation.

TABLE XXV—Continued

AMINO ACIDS—Continued

Name of Compound	Decomposition Point	Derivatives			
		Benzoyl	Phenyl-urea	p-Toluenesulfonyl	Miscellaneous
<i>dl</i> -Phenylalanine . . .	273°	188°	182°	135°	Picrolonate . . 182°
<i>l</i> -Histidine	277	204	Picrate 86
<i>d</i> - or <i>l</i> -Isoleucine . . .	279	117	120	132	Picrolonate . . 170
α -Aminoisobutyric acid	280
<i>dl</i> -Aspartic acid . . .	280	165
<i>l</i> -Dihydroxyphenylalanine	280
<i>l</i> -Methionine	283	α -Naphthyl-urea 186
5-Aminosalicylic acid	283	252	Acetyl 218
<i>d</i> - α -Amino- <i>n</i> -butyric acid	285	121	α -Naphthyl-urea 195
<i>d</i> -Norleucine	285
<i>l</i> -Tryptophane	289	166	176	α -Naphthyl-urea 158
<i>dl</i> -Isoleucine	292	118	140
<i>dl</i> -Alanine	295	166	190	139	Picrolonate . . 214
<i>d</i> - or <i>l</i> -Alanine	297	151	168	133	α -Naphthyl-urea 198
<i>dl</i> -Valine	298	132	163	Formyl 145
<i>dl</i> - α -Amino- <i>n</i> -butyric acid	307	147	170	α -Naphthyl-urea 194
<i>d</i> - or <i>l</i> -Valine	315	147	147	Formyl 156
<i>dl</i> -Tyrosine	318	197	Picrolonate . . 260
<i>d</i> - or <i>l</i> -Phenylalanine	320	146	181	161	Formyl 167
<i>dl</i> -Norleucine	327	124	Formyl 114
<i>dl</i> -Leucine	332	141	165	Picrolonate . . 150
<i>d</i> - or <i>l</i> -Leucine	337	107	115	122
<i>l</i> -Tyrosine	344	166	104	114	α -Naphthyl-urea 205
<i>dl</i> -Ornithine	267d.	192	Picrate 195
<i>d</i> - or <i>l</i> -Ornithine	240d.	190	Picrate 204
<i>dl</i> -Lysine	249	196	Dibenzoyl . . 146
<i>dl</i> -Isoleucine	151	184
<i>l</i> -Isoleucine	109

TABLE XXVI

CARBOHYDRATES AND GLYCOSIDES*

Name of Compound	Decomposition Point	Specific Rotation in Water at 20°	Time Required for Osazone Formation (Min.)	Derivatives	
				Osazone	Acetate
Raffinose (hydrated).	80°	+104.5			99°
Glucose (hydrated) . .	90	+ 47.7	4 to 5	205°	{ 132 (β) 112 (α)
<i>D</i> -Ribose.	95	- 21.5		166	
Maltose (hydrated) . .	100	+129.0		206	158
Levulose (<i>D</i> -Fructose)	104	- 92.0	2	205	{ 109 (β) 70 (α)
<i>L</i> -Rhamnose.	105	+ 9.4		182	
<i>L</i> -Lyxose.	105	+ 13.5		163	
Raffinose (anhydrous)	119	+123			99
<i>D</i> -Mannose.	132	+ 14.1	0.5	205	
<i>dl</i> -Glyceraldehyde. . .	142 †			132	{ (dimeride) 154
<i>D</i> -Xylose.	145	+ 18.7	7	163	141
Glucose (anhydrous) .	146	+ 52.8	4 to 5	205	{ 132 (β) 112 (α)
Melezitose.	147	+ 8			
<i>L</i> -Arabinose.	160	+104	10	166	
<i>dl</i> -Arabinose.	164			169	
α-Methylglucoside. . .	165	+157.6			101
Arbutin (hydrated) . .	165	- 60.3			136
Maltose.	165	+129		206	158
<i>dl</i> -Ascorbic acid. . . .	169				
<i>d</i> -Ascorbic acid.		- 48			
<i>l</i> -Ascorbic acid.		+ 49			
<i>D</i> -Galactose.	170	+ 81.7	15	201	{ 142 (β) 95 (α)
Helicin.	175	- 60.4			
Inulin.	178	- 39.5	25		
Populin.	180				
Sucrose.	185	+ 66.5	30	205	89
Coniferin.	185	- 66.9			125
α-Methylmannoside. .	193	+ 79.2			
Salicin.	201	- 62.4			130
Lactose.	203	+ 52.5		200d.	100
Amygdalin.	214	- 41			166
Cellobiose.	225	+ 35.0		198	
Glycogen.	240	198			
Cellulose acetate. . .	d.				
Cellulose.	d.				
Starch.	d.				

* A capital *D* or *L* indicates configuration when placed before the name of the sugar.

† Melts without decomposition.

TABLE XXVII
ESTERS (LIQUIDS)

Name of Compound	B. P.	Sp. Gr.	Name of Compound	B. P.	Sp. Gr.
Methyl formate.....	32°	0.998 ⁰ / ₄	Ethyl crotonate....	138°	0.9175 ²⁰ / ₄
Ethyl formate.....	54	0.938	Isoamyl acetate....	142	0.884
Methyl acetate.....	57	0.958	<i>n</i> -Propyl <i>n</i> -butyrate	143	0.893
Isopropyl formate....	68	0.883	<i>n</i> -Butyl propionate.	144	0.895
Vinyl acetate.....	72		Methyl lactate.....	144	1.090 ¹⁹ / ₄
Methyl chloroform- ate.....	75	1.236 ¹⁵ / ₄	Methyl bromoace- tate.....	144d.	1.657 ¹⁹ / ₄
Ethyl acetate.....	77	0.924	Ethylene glycol monomethyl		
Methyl propionate...	79	0.937	ether acetate.....	144	1.0067 ²⁰ / ₂₀
<i>n</i> -Propyl formate....	81	0.918	Ethyl <i>n</i> -valerate....	145	0.8785 ²⁰ / ₄
Allyl formate.....	83	0.932 ¹⁷ / ₄	<i>n</i> -Butyl chloroform- ate.....	145	1.078
Methyl acrylate.....	85	0.977 ⁰ / ₄	Ethyl chloroacetate.	145	1.158
Methyl carbonate....	90	1.065 ¹⁷ / ₄	Ethyl orthoformate.	145	0.897
Isopropyl acetate....	91	0.917	β -Chloroethyl ace- tate.....	145	1.178
Methyl isobutyrate...	92	0.912 ⁰ / ₄	<i>n</i> -Amyl acetate.....	146	0.896
Ethyl chloroformate.	93	1.144 ¹⁵ / ₄	Ethyl α -chloropro- pionate.....	146	1.087
<i>sec</i> -Butyl formate....	97	0.882	Benzyl chloroacetate	147	1.222 ⁴ / ₄
Isobutyl formate....	98	0.905	Isobutyl isobutyrate	147	0.875
Ethyl propionate....	98	0.912	Methylisobutylcar- binol acetate.....	148	0.8805 ⁰ / ₄
<i>n</i> -Propyl acetate.....	101	0.909	Methyl <i>n</i> -caproate..	150	0.904
Ethyl acrylate.....	101	0.925 ⁰ / ₄	Ethyl lactate.....	152	1.031 ¹⁹ / ₄
Methyl orthoformate	101	0.974 ²⁰ / ₄	Ethylethoxyacetate	152	
Methyl <i>n</i> -butyrate...	102	0.919	Isoamyl chloroform- ate.....	154	1.032 ¹⁵ / ₄
Allyl acetate.....	103	0.938	Ethyl pyruvate.....	155	1.080 ¹⁴ / ₄
Isopropyl chloro- formate.....	105		Ethylene glycol monoethyl ether		
<i>n</i> -Butyl formate.....	107	0.911	acetate.....	156	0.9749 ²⁰ / ₂₀
Ethyl isobutyrate....	110	0.890	Isobutyl <i>n</i> -butyrate.	157	0.888
Chloromethyl acetate	111	1.195 ¹⁴ / ₄	Ethyl dichloroacetate	158	1.282
<i>sec</i> -Butyl acetate....	111	0.870	Ethyl bromoacetate	159	1.506
<i>n</i> -Propyl chloroform- ate.....	113	1.094 ¹⁵ / ₄	Isoamyl propionate.	160	0.888
Isobutyl acetate.....	116	0.892	Ethyl glycolate....	160	1.0869 ¹⁵ / ₄
Methyl isovalerate...	116	0.901	Cyclohexyl formate.	162	1.010
Ethyl <i>n</i> -butyrate....	120	0.900	Ethyl α -bromopropi- onate.....	162	1.329
<i>n</i> -Propyl propionate.	122	0.902	β -Bromoethyl ace- tate.....	163	1.524
Isoamyl formate.....	123	0.894	<i>n</i> -Butyl <i>n</i> -butyrate.	165	0.888
<i>n</i> -Butyl acetate.....	125	0.902	Ethyl <i>n</i> -caproate...	166	0.889
Ethyl carbonate....	126	0.976	Ethyl trichloroace- tate.....	167	1.369 ¹⁵ / ₄
Isopropyl <i>n</i> -butyrate.	128	0.879 ⁰ / ₄	<i>n</i> -Propyl <i>n</i> -valerate.	167	0.8888 ⁰ / ₄
Methyl <i>n</i> -valerate...	130	0.910	<i>n</i> -Propyl carbonate.	168	0.949 ¹⁷ / ₄
Isobutyl chloroform- ate.....	130	1.053 ¹⁵ / ₄			
Bromomethyl acetate	130	1.656 ¹² / ₄			
Methyl chloroacetate	130	1.238			
<i>n</i> -Amyl formate.....	130	0.902			
Ethyl isovalerate....	134	0.865			
Methyl pyruvate....	136	1.154			
Isobutyl propionate.	137	0.888			

TABLES OF DERIVATIVES

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TABLE XXVII—Continued

ESTERS (LIQUIDS)—Continued

Name of Compound	B. P.	Sp. Gr.	Name of Compound	B. P.	Sp. Gr.
Isopropyl lactate....	168°	<i>o</i> -Cresyl acetate....	208°	1.048 ¹⁹ / ₄
Methyl acetoacetate....	169	1.081 ¹⁵ / ₄	Trimethylene glycol diacetate....	210	1.070 ¹⁹ / ₄
Methyl <i>n</i> -heptoate....	173	0.898	Phenyl propionate...	211	1.054 ¹⁵ / ₄
Cyclohexyl acetate....	175	0.972 ¹⁹ / ₄	<i>n</i> -Propyl furoate....	211	1.0745 ²⁶ / ₄
<i>n</i> -Butyl chloroacetate....	175	1.081 ¹⁵ / ₄	Ethylene glycol di- propionate....	212	1.045 ²⁵ / ₄
Furfuryl acetate....	176	1.1176 ²⁰ / ₂₀	<i>m</i> -Cresyl acetate....	212
Isoamyl <i>n</i> -butyrate....	178	0.882	<i>p</i> -Cresyl acetate....	212	1.050 ²³ / ₄
Ethyl β -bromopropionate....	179	1.425	<i>n</i> -Propyl oxalate....	213	1.038
Methyl furoate....	181	1.1786 ²¹ / ₄	Methyl pelargonate	213	0.892
Methyl malonate....	181	1.160 ¹⁵ / ₄	Ethyl benzoate....	213	1.066
Ethyl acetoacetate....	181	1.031 ¹⁶ / ₄	Methyl <i>o</i> -toluate....	213	1.073 ¹⁵ / ₄
β -Hydroxyethyl acetate....	182	Methyl <i>m</i> -toluate....	215	1.066 ¹⁵ / ₄
<i>n</i> -Amyl <i>n</i> -butyrate....	185	0.8832 ⁰ / ₀	Ethyl fumarate....	215	1.0472 ²⁵ / ₄
<i>n</i> -Propyl <i>n</i> -caproate....	186	0.8844 ⁰ / ₀	Benzyl acetate....	216	1.062 ¹⁵ / ₄
Ethyl oxalate....	186	1.082	Ethyl succinate....	216	1.049 ¹⁵ / ₄
Ethyl methylacetate....	187	1.024 ¹⁵ / ₄	Methyl <i>p</i> -toluate....	217
Ethyl <i>n</i> -heptoate....	189	0.888	Diethylene glycol monoethyl ether acetate....	218	1.0114 ²⁰ / ₂₀
Ethylene glycol diacetate....	190	1.128	Isopropyl benzoate....	218	1.023
Isopropyl oxalate....	190	1.010 ¹⁸ / ₄	Methyl phenylacetate....	218	1.044 ¹⁶ / ₄
Isobutyl carbonate....	190	0.919 ¹⁵ / ₄	<i>n</i> -Propyl levulinate....	221	0.9895 ²⁰ / ₄
Isoamyl isovalerate....	190	0.870	Methyl salicylate....	224	1.184 ²⁰ / ₄
Methyl levulinate....	191	1.068	Ethyl maleate....	225	1.074 ¹⁵ / ₄
<i>n</i> -Heptyl acetate....	192	0.8891 ⁰ / ₀	Ethyl pelargonate....	227	0.866 ¹⁷ / ₄
Methyl caprylate....	193	0.894	Phenyl <i>n</i> -butyrate....	227	1.027 ¹⁵ / ₄
Tetrahydrofurfuryl acetate....	194	1.0624 ²⁵ / ₄	<i>l</i> -Menthyl acetate....	227	0.9185 ²⁰ / ₄
Methyl succinate....	195	1.120 ¹⁵ / ₄	Isoamyl carbonate....	228	0.912 ¹⁴ / ₄
Ethyl methylmalonate....	196	1.019 ¹⁵ / ₄	Isobutyl oxalate....	229	1.002 ¹⁴ / ₄
Phenyl acetate....	196	1.081 ¹⁵ / ₄	Ethyl phenylacetate	229	1.031
Ethyl malonate....	198	1.077	<i>n</i> -Propyl benzoate....	230	1.025 ¹⁵ / ₄
Methyl benzoate....	198	1.103	Allyl benzoate....	230	1.067 ⁴ / ₄
2-Ethyl-1-hexyl acetate....	199	0.8733 ²⁰ / ₂₀	Methyl <i>m</i> -chlorobenzoate....	231
Methyl cyanoacetate....	200	1.0962 ²⁵ / ₄	Methyl caprate....	232	0.876 ¹⁸ / ₄
Benzyl formate....	203	1.081 ²³ / ₄	Methyl <i>o</i> -chlorobenzoate....	234
<i>n</i> -Amyl valerate....	204	0.881 ⁰ / ₄	Ethyl salicylate....	234	1.147 ⁴ / ₄
γ -Butyrolactone....	204	Ethyl bromomalonate....	235	1.426 ¹⁵ / ₁₅
Ethyl levulinate....	205	1.016	Isopropyl salicylate....	237	1.095 ¹⁹ / ₄
Ethyl caprylate....	206	0.887	Benzyl <i>n</i> -butyrate....	238	1.033 ¹⁵ / ₄
<i>n</i> -Butyl carbonate....	207	0.941 ⁰ / ₄	<i>n</i> -Propyl salicylate....	239	1.098 ¹⁵ / ₄
γ -Valerolactone....	207	1.0465 ¹⁵ / ₄	Ethyl <i>n</i> -butylmalonate....	240
			Isobutyl benzoate....	241	1.002 ¹⁵ / ₄

TABLE XXVII—Continued
ESTERS (LIQUIDS)—Continued

Name of Compound	B. P.	Sp. gr.	Name of Compound	B. P.	Sp. gr.
<i>n</i> -Butyl oxalate.....	243°	1.010	Ethyl laurate.....	269°	0.867 ¹³ / ₄
Thymyl acetate.....	244	1.009	Ethyl benzoylace-		
Methyl <i>o</i> -bromoben-			tate.....	270d.	1.1219 ¹⁵ / ₄
zoate.....	244		Ethyl cinnamate...	271	1.050
Ethyl adipate.....	245		Isoamyl salicylate...	277	1.065 ¹⁵ / ₄
Ethyl caprate.....	245	0.868 ¹⁸ / ₄	Resorcinol diacetate.	278	1.180 ¹⁹ / ₄
<i>n</i> -Propyl succinate...	246	1.016 ⁴ / ₄	Methyl <i>m</i> -nitroben-		
Diethylene glycol			zoate.....	279	
mono- <i>n</i> -butylether			<i>d</i> -Ethyl tartrate....	280	1.199
acetate.....	246	0.9871 ²⁰ / ₂₀	Methyl phthalate...	282	1.196 ¹⁹ / ₄
Isobutyl phenylace-			Ethyl suberate.....	282	0.9822 ²⁰ / ₄
tate.....	247	0.999 ¹⁸ / ₄	Glyceryl tripropion-		
Methyl undecylen-			ate.....	289	1.083 ¹⁹ / ₄
ate.....	248		Ethyl azelate.....	291	0.9766 ¹⁵ / ₀
<i>n</i> -Butyl benzoate....	249	1.000	Ethyl citrate.....	294	1.137
Ethyl acetonediacar-			Methyl myristate...	296	0.873 ¹⁹ / ₄
boxylate.....	250	1.113	Isoamyl succinate...	297	0.961 ¹³ / ₄
<i>n</i> -Butyl phenylace-			Ethyl phthalate....	298	1.117
tate.....	254	0.996 ¹⁸ / ₄	Ethyl benzylmaloi-		
Ethyl pimelate.....	255	0.9945 ²⁰ / ₄	nate.....	300	1.077 ¹⁵ / ₄
Ethyl benzoylform-			Isopropyl phthalate.	302	1.065 ¹⁹ / ₄
ate.....	257		Ethyl myristate....	306	0.865 ¹⁹ / ₄
Glyceryl triacetate...	258	1.161 ¹⁵ / ₄	Ethyl sebacate.....	307	0.965 ¹⁶ / ₄
Isoamyl oxalate.....	262	0.968 ¹¹ / ₄	<i>o</i> -Cresyl benzoate...	307	1.114 ¹⁹ / ₄
Isoamyl benzoate...	262	1.004	Glyceryl tributyrat	318	1.033 ¹⁷ / ₄
Isobutyl succinate...	265	0.974	Benzyl salicylate...	320	
Methyl laurate.....	268	0.869 ¹⁹ / ₄	Benzyl benzoate...	323	1.114 ¹⁸ / ₄
<i>n</i> -Butyl salicylate...	268	1.074 ¹⁹ / ₄	<i>n</i> -Butyl phthalate...	338	1.050 ¹⁹ / ₄
Ethyl anisate.....	269	1.119 ⁴ / ₄	Isoamyl phthalate...	349	1.024 ¹⁷ / ₄

TABLE XXVII—Continued
ESTERS (SOLIDS)*

Name of Compound	M. P.	B. P.	Name of Compound	M. P.	B. P.
Methyl laurate.....	5°	268°	Methyl palmitate...	30°	
Ethyl anisate.....	7	269	Methyl <i>m</i> -bromoben-		
Ethyl myristate.....	11	306	zoate.....	32	
<i>d</i> -Ethyl tartrate.....	17	280	Methyl <i>p</i> -toluate...	33	217°
Methyl myristate...	18	323	Thymyl benzoate...	33	
Methyl succinate...	19	195	Ethyl stearate.....	33	
Phenyl propionate...	20	211	Ethyl furoate.....	33	
Methyl <i>m</i> -chloroben-			Methyl cinnamate...	36	263
zoate.....	21	231	Ethyl mandelate...	37	254
Cetyl acetate.....	22		Methyl sebacate...	38	288d.
<i>d</i> - <i>n</i> -Butyl tartrate...	22		Methyl stearate...	38	
Ethyl palmitate....	24		Benzyl cinnamate...	39	
Bornyl acetate.....	29	221	Benzyl phthalate...	42	

* Many solid esters are listed as derivatives of acids, alcohols and phenols (Tables XIX, XX and XLII).

TABLE XXVII—Continued
ESTERS (SOLIDS)*—Continued

Name of Compound	M. P.	B. P.	Name of Compound	M. P.	B. P.
Phenyl salicylate....	42°		Methyl <i>m</i> -nitrobenzoate....	78°	
Benzyl succinate....	42		Phenyl carbonate....	78	306°
Cyclohexyl oxalate....	42		Methyl citrate....	79	285d.
Methyl <i>p</i> -Chlorobenzoate....	44		Benzyl oxalate....	80	
Cinnamyl cinnamate....	44		Methyl <i>p</i> -bromobenzoate....	81	
Methyl anisate....	45	255°	Guaiacol carbonate....	86	
Ethyl <i>m</i> -nitrobenzoate....	47	296	Ethyl 3,5-dinitrobenzoate....	94	
<i>d</i> -Methyl tartrate....	48(61)	280	β -Naphthyl salicylate....	95	
α -Naphthyl acetate....	49		Methyl <i>p</i> -nitrobenzoate....	96	
Methyl oxalate....	51	163	β -Naphthyl benzoate....	107	
<i>m</i> -Cresyl benzoate....	54		Methyl 3,5-dinitrobenzoate....	108	
Ethyl <i>p</i> -nitrobenzoate....	56		<i>m</i> -Cresyl carbonate....	115	
Methyl mandelate....	58		Ethyl <i>p</i> -hydroxybenzoate....	116	
<i>o</i> -Cresyl carbonate....	60		Resorcinol dibenzoate....	117	
Ethyl trichloroacetate....	66	162	Hydroquinone diacetate....	123	
Coumarin....	67	290	Methyl <i>m</i> -nitrocinamate....	124	
Phenyl benzoate....	68	299	Lactide....	128	255
Phenyl phthalate....	70		Methyl <i>p</i> -hydroxybenzoate....	131	
Methyl <i>m</i> -hydroxybenzoate....	70		Ethyl <i>p</i> -nitrocinamate....	137	
β -Naphthyl acetate....	70		Methyl terephthalate....	140	
Glyceryl tristearate....	71		Pyrogallol triacetate....	161	
<i>p</i> -Cresyl benzoate....	71		Methyl <i>p</i> -nitrocinamate....	161	
Phenyl cinnamate....	72				
Ethyl <i>m</i> -hydroxybenzoate....	72	282			
Ethylene glycol dibenzoate....	73				
Phthalide....	73	290			
Methyl <i>o</i> -nitrocinamate....	73				

* Many solid esters are listed as derivatives of acids, alcohols and phenols (Tables XIX, XX and XLII).

ESTERS OF INORGANIC ACIDS

Name of Compound	B. P.	Sp. Gr.	Name of Compound	B. P.	Sp. Gr.
<i>Nitrites</i>			<i>Nitrates—Continued</i>		
Ethyl nitrite....	17°	0.900 ¹⁵ / ₄	Ethyl nitrate....	87°	1.130 ⁴ / ₄
<i>n</i> -Propyl nitrite....	44	0.998	<i>n</i> -Propyl nitrate....	110	1.075 ⁹ / ₄
Isobutyl nitrite....	67	0.888 ⁴ / ₄	Isobutyl nitrate....	123	1.033 ⁴ / ₄
<i>n</i> -Butyl nitrite....	75	0.911	<i>n</i> -Butyl nitrate....	136	1.048
Isoamyl nitrite....	99	0.880 ¹⁵ / ₄	Isoamyl nitrate....	147	1.000 ⁷ / ₄
<i>n</i> -Amyl nitrite....	104	0.8528 ²⁰ / ₄	<i>Sulfates</i>		
<i>Nitrates</i>			Methyl sulfate....	188	1.321 ²⁵ / ₄
Methyl nitrate....	65	1.232 ⁵ / ₄	Ethyl sulfate....	208	1.172 ²⁵ / ₄

TABLE XXVIII

ETHERS—ALIPHATIC

Name of Compound	B. P.	Sp. Gr.	Melting Point of Alkyl 3,5-Dinitro- benzoate
Methyl ethyl ether.....	10°	0.7252 ⁹ / ₀
Furan.....	32	0.8644 ⁹ / ₀
Ethyl ether.....	35	0.718 ¹⁵ / ₄	93°
Chloromethyl ether.....	59	1.020 ¹⁰ / ₄
Allyl ethyl ether.....	65
Isopropyl ether.....	68	0.724	122
Chloromethyl ethyl ether.....	80
<i>n</i> -Propyl ether.....	90	0.744 ²⁰ / ₀	74
Ethyl <i>n</i> -butyl ether.....	92	0.7522 ²⁰ / ₂₀
α -Chloroethyl ether.....	98
Dioxane.....	102	1.0353 ²⁰ / ₂₀
α,α' -Dichloromethyl ether.....	105	1.328 ¹⁵ / ₄
β -Chloroethyl ether.....	107	1.067 ⁹ / ₄
α,α' -Dichloroethyl ether.....	116	1.138 ¹² / ₄
Epichlorohydrin.....	117	1.204 ⁰ / ₄
Ethylene glycol diethyl ether.....	121	0.8424 ²⁰ / ₂₀
Isobutyl ether.....	122	0.762 ¹⁵ / ₄	86
β -Bromoethyl ether.....	127	1.370 ⁰ / ₄
Ethylene glycol monoethyl ether.....	135	0.9311 ²⁰ / ₂₀
<i>n</i> -Butyl ether.....	140	0.769	64
α,β -Dichloroethyl ether.....	140	1.174 ²³ / ₄
Dibromomethyl ether.....	150	2.201
Benzyl methyl ether.....	167	0.981 ⁴ / ₄
Ethylene glycol mono- <i>n</i> -butyl ether.....	171	0.902 ²⁰ / ₂₀
Isoamyl ether.....	172	0.774 ²⁵ / ₂₅	62
Cincole.....	176	0.927
β,β' -Dichloroethyl ether.....	179	1.23 ¹⁵ / ₁₅
Diethylene glycol diethyl ether.....	188	0.908 ²⁰ / ₂₀
Ethyl benzyl ether.....	189	0.949 ²⁰ / ₄
<i>n</i> -Amyl ether.....	190	46
Diethylene glycol monomethyl ether.....	193	1.0354 ²⁰ / ₂₀
Diethylene glycol monoethyl ether.....	202	0.9902 ²⁰ / ₂₀
<i>n</i> -Hexyl ether.....	208	58
Benzyl isobutyl ether.....	212
Benzyl <i>n</i> -butyl ether.....	212
γ,γ' -Dichloropropyl ether.....	215	1.140
Diethylene glycol mono- <i>n</i> -butyl ether.....	231	0.9954 ²⁰ / ₂₀
Ethylene glycol monophenyl ether.....	245	1.1094 ²⁰ / ₂₀
<i>n</i> -Heptyl ether.....	260	0.815 ⁰ / ₄	47
Benzyl ether.....	298	1.036 ¹⁵ / ₄	112

TABLE XXIX

ETHERS—AROMATIC (LIQUIDS)

Name of Compound	B. P.	Sp. Gr.	Picrate	Other Derivatives
Anisole.....	154°	0.988	81°	Dinitro..... 87°
<i>o</i> -Cresyl methyl ether.....	171	0.966 ⁹ / ₄	119	Bromo..... 63
Phenetole.....	172	0.979 ⁹ / ₄	92	Nitro..... 58
<i>p</i> -Cresyl methyl ether.....	176	0.987 ⁹ / ₄	89	Anisic acid..... 184
<i>m</i> -Cresyl methyl ether.....	177	0.985 ⁹ / ₄	114	Trinitro..... 91
<i>o</i> -Cresyl ethyl ether.....	192	118	Dinitro..... 51
<i>m</i> -Cresyl ethyl ether.....	192	115	<i>m</i> -Ethoxybenzoic acid..... 137
<i>p</i> -Cresyl ethyl ether.....	192	111	<i>p</i> -Ethoxybenzoic acid..... 195
<i>o</i> -Chloroanisole.....	195	Nitro..... 95
<i>p</i> -Chloroanisole.....	200	Nitro..... 98
Guaiacol.....	205	89
Veratrole.....	206	1.086 ¹⁵ / ₄	57	Dibromo..... 92
<i>o</i> -Chlorophenetole.....	208	Nitro..... 82
<i>n</i> -Butyl phenyl ether.....	210	0.950	112
<i>p</i> -Chlorophenetole.....	212	Dinitro..... 54
Resorcinol dimethyl ether	214	1.080 ⁹ / ₄	58	Dibromo..... 140
.....	Trinitro..... 124
Methyl thymyl ether.....	216	0.954 ⁹ / ₄	Trinitro..... 92
<i>o</i> -Bromoanisole.....	218	Nitro..... 106
<i>n</i> -Butyl <i>o</i> -cresyl ether.....	223	0.944 ⁹ / ₄
<i>p</i> -Bromoanisole.....	223	1.494 ⁹ / ₄	Nitro..... 88
<i>o</i> -Bromophenetole.....	224	Nitro..... 98
<i>p</i> -Bromophenetole.....	229	Nitro..... 47
Safrole.....	232	1.096 ¹⁸ / ₄	105	Pentabromo..... 169
Anethole.....	232	0.989 ²⁸ / ₄	70	Tribromo..... 108
Resorcinol diethyl ether..	235	58
<i>o</i> -Iodoanisole.....	240	1.800	Nitro..... 95
Eugenol methyl ether.....	244	1.055 ¹⁵ / ₄	114	Tribromo..... 78
<i>o</i> -Iodophenetole.....	245	Nitro..... 96
Isosafrole.....	246	1.125 ¹⁴ / ₄	75	Tribromo..... 109
Phenyl ether.....	252	1.073	110	Dibromo..... 58
Methyl α -naphthyl ether..	265	1.096 ¹⁴ / ₄	113	Bromo..... 46
Ethyl α -naphthyl ether...	278	1.074	100	4-Bromo..... 48
Ethyl β -naphthyl ether...	282	1.064	44	1-Bromo..... 66

TABLES OF DERIVATIVES

TABLE XXIX—Continued

ETHERS—AROMATIC (SOLIDS)

Name of Compound	M. P.	Picrate	Other Derivatives
Veratrole.....	21°	57°	Nitro..... 95°
<i>p</i> -Chlorophenetole.....	21	Dinitro..... 54
Anethole.....	22	70	Tribromo..... 108
Isoamyl β -naphthyl ether.....	26	91
<i>p</i> -Iodophenetole.....	27	Nitro..... 96
Phenyl ether.....	28	110	Dinitro..... 135
.....	Dibromo..... 54
β -Bromoethyl phenyl ether.....	32	Bromo..... 56
Apiole.....	32	Apiolic acid..... 175
<i>o</i> -Methoxybiphenyl.....	32	Nitro..... 95
Ethyl β -naphthyl ether.....	37	44	Bromo..... 66
2,4,6-Trichlorophenetole.....	43	Dinitro..... 100
Catechol diethyl ether.....	43	71	Trinitro..... 122
Hydroquinone dimethyl ether.....	55	119	Dibromo..... 142
Phenoxthin.....	59
2,4,6-Trichloroanisole.....	60	Dinitro..... 95
Methyl β -naphthyl ether.....	72	108	Bromo..... 62
Hydroquinone diethyl ether.....	72	Trinitro..... 130
2,4,6-Tribromophenetole.....	72	Nitro..... 79
Benzyl α -naphthyl ether.....	77
<i>p</i> -Methoxybiphenyl.....	85
2,4,6-Tribromoanisole.....	87
Dibenzofuran.....	87	94	Nitro..... 182
3,5-Dinitroanisole.....	106
Hydroquinone dibenzyl ether.....	127	Nitro..... 83

TABLE XXX

HALIDES—ALKENYL

Name of Compound	B. P.	Sp. Gr.	Derivatives	
			Anilide	Alkenyl-mercuric Halide
Vinyl bromide.....	16°	1.517 ¹⁴ / ₄	104°
2-Chloropropene.....	30	0.918 ⁹ / ₄
1-Chloropropene.....	36	114
Allyl chloride.....	46	0.938	*
2-Bromopropene.....	48	1.362
Vinyl iodide.....	56	2.080 ⁰ / ₄
Chloroprene.....	59	0.958 ²⁰ / ₂₀
1-Bromopropene.....	60	1.428	114
Allyl bromide.....	71	1.398	*
Allyl iodide.....	103	1.848 ¹² / ₁₂	*
β -Chlorostyrene.....	199	1.112 ¹⁵ / ₄	115
β -Bromostyrene.....	221	1.427	115	91°

* Cretonanilide 114°.

TABLE XXXI
HALIDES—ALKYL AND CYCLOALKYL

Name of Compound	B. P.	Derivatives		
		Anilide	α -Naphthalide	Alkylmercuric Halide
<i>Chlorides:</i>				
Ethyl.....	12°	104°	126°	192°
Isopropyl.....	36	103		
n-Propyl.....	46	92	121	147
tert-Butyl.....	51	128	147	
sec-Butyl.....	67	108	129	
Isobutyl.....	68	109	125	
n-Butyl.....	77	63	112	127
tert-Amyl.....	86	92	138	
Isoamyl.....	100	108	111	86
n-Amyl.....	107	96	112	110
n-Hexyl.....	134	69	106	125
Cyclohexyl.....	142	146	188	
n-Heptyl.....	160	57	95	119
Benzyl.....	179	117	166	
n-Octyl.....	184	57	91	
β -Phenylethyl.....	190	97		
α -Phenylethyl.....	195	133		
Bornyl.....	207			
Cetyl.....	289d.			102
<i>Bromides:</i>				
Methyl.....	5	114	160	160
Ethyl.....	38	104	126	133
Isopropyl.....	60	103		93
n-Propyl.....	71	92	121	138
tert-Butyl.....	72	128		
sec-Butyl.....	90	108		39
Isobutyl.....	91	109	125	55
n-Butyl.....	100	63	112	129
tert-Amyl.....	108	92		
Isoamyl.....	118	108		80
2-Pentyl.....	118	93	104	
3-Pentyl.....	119	121		
n-Amyl.....	129	96	112	122
n-Hexyl.....	157	69	106	118
Cyclohexyl.....	165	146	188	153
n-Heptyl.....	174	57	95	118
Benzyl.....	198	117	166	119
n-Octyl.....	204	57	91	109
α -Phenylethyl.....	205			
β -Phenylethyl.....	218	97		169
<i>Iodides:</i>				
Methyl.....	43	114	160	145
Ethyl.....	72	104	126	182
Isopropyl.....	89	103		
tert-Butyl.....	98	128		
n-Propyl.....	102	92	121	112
sec-Butyl.....	119	108		
Isobutyl.....	120	109	125	72
tert-Amyl.....	128	92		
n-Butyl.....	130	63	112	117
Isoamyl.....	148	108		122
n-Amyl.....	156	96	112	110
n-Hexyl.....	180	69	106	110
n-Heptyl.....	204	57	95	102

TABLE XXXII

HALIDES—HALOGEN DERIVATIVES OF AROMATIC HYDROCARBONS (LIQUIDS)

Name of Compound	B. P.	Derivatives			
		Nitration Product		Miscellaneous	
		Position	M. P.	Compound	M. P.
Fluorobenzene	85°			Sulfone	98°
<i>o</i> -Fluorotoluene	114				
<i>m</i> -Fluorotoluene	115				
<i>p</i> -Fluorotoluene	117				
Chlorobenzene	132	2, 4	52*		
Bromobenzene	157	2, 4	75	α -Naphthalide	161
<i>o</i> -Chlorotoluene	159	3, 5	63	<i>o</i> -Chlorobenzoic acid	140
<i>m</i> -Chlorotoluene	162	4, 6	91	<i>m</i> -Chlorobenzoic acid	158
<i>p</i> -Chlorotoluene	162	2	38	<i>p</i> -Chlorobenzoic acid	242
<i>m</i> -Dichlorobenzene	172	4, 6	103		
<i>o</i> -Dichlorobenzene	179	4, 5	110		
<i>o</i> -Bromotoluene	181	3, 5	82	<i>o</i> -Bromobenzoic acid	147
<i>p</i> -Chloroethylbenzene	182				
<i>m</i> -Bromotoluene	183	4, 6	103	<i>m</i> -Bromobenzoic acid	155
<i>p</i> -Bromotoluene	185	2	47	<i>p</i> -Bromobenzoic acid	251
Iodobenzene	188	4	171	<i>p</i> -Bromiodobenzene	91
2,4-Dichlorotoluene	195	3, 5	104	2,4-Dichlorobenzoic acid	160
<i>m</i> -Iodotoluene	204			<i>m</i> -Iodobenzoic acid	186
<i>o</i> -Iodotoluene	211	6	103	<i>o</i> -Iodobenzoic acid	162
<i>p</i> -Iodotoluene	211			<i>p</i> -Iodobenzoic acid	265
1,2,4-Trichlorobenzene	213	5	56		
<i>m</i> -Dibromobenzene	219	4	61		
<i>o</i> -Dibromobenzene	224	4, 5	114		
Bromomesitylene	225				
2-Bromocymene	234	?, ?	97	Anilide	143
3,4-Dibromotoluene	241			3,4-Dibromobenzoic acid	233
α -Chloronaphthalene	263	4, 5	180	Picrate	137
α -Bromonaphthalene	279	4	85		

* Metastable forms melting at 27° and 43° are also reported.

TABLE XXXII—Continued

HALIDES—HALOGEN DERIVATIVES OF AROMATIC HYDROCARBONS (SOLIDS)

Name of Compound	M. P.	Derivatives			
		Nitration Product		Miscellaneous	
		Position	M. P.	Compound	M. P.
<i>p</i> -Bromotoluene.....	28°	2	47°	<i>p</i> -Bromobenzoic acid.	251°
2-Chlorobiphenyl.....	34			<i>o</i> -Chlorobenzoic acid..	140
<i>p</i> -Iodotoluene.....	35			<i>p</i> -Iodobenzoic acid...	265
1,2,4-Tribromobenzene	44				
1,2,3-Trichlorobenzene	52	4	56		
<i>p</i> -Dichlorobenzene....	53	2	54		
β -Iodonaphthalene....	55			Anilide.....	170
β -Chloronaphthalene..	56	1, 8	175	Picrate.....	81
β -Bromonaphthalene..	59			Anilide.....	170
1,3,5-Trichlorobenzene	63	2	68		
1,2-Dibromonaphthalene.....	67			3,4-Dibromophthalic acid.....	196
<i>p</i> -Bromochlorobenzene	67	2	72		
4-Chlorobiphenyl.....	77				
1,4-Dibromonaphthalene.....	82			3,6-Dibromophthalic acid.....	135
1,2,3-Tribromobenzene	87				
<i>p</i> -Dibromobenzene....	89	2, 5	84		
4-Bromobiphenyl.....	89				
1,3,5-Tribromobenzene	120				
<i>p</i> -Diiodobenzene.....	129			<i>p</i> -Iodonitrobenzene...	171
1,2,4,5-Tetrachlorobenzene.....	138				
4,4'-Dibromobiphenyl.	169				
1,2,4,5-Tetrabromobenzene.....	180	3	168		
Naphthalene tetrachloride.....	182			1,3-Dichloronaphthalene.....	61
Hexachlorobenzene...	229			Chloranil.....	290

TABLE XXXIII

HALIDES—POLYHALOGEN DERIVATIVES OF NON-BENZENOID HYDROCARBONS
(LIQUIDS)

Name of Compound	B. P.	Sp. Gr.	n_D
Methylene chloride	42°	1.378 ⁹ / ₄	1.4237
Dichloroethylene (<i>cis</i>)	48	1.265 ¹⁶ / ₄	1.4490
Dichloroethylene (<i>trans</i>)	60	1.291 ¹⁵ / ₄	1.4518
Ethylidene chloride	60	1.180 ²² / ₄	1.4166
Chloroform	61	1.504 ¹² / ₄	1.4467
2,2-Dichloropropane	70	1.093	1.4093
1,1,1-Trichloroethane	74	1.325 ²⁶ / ₄	1.4349
Carbon tetrachloride	78	1.591 ²⁵ / ₂₅	1.4607
1-Bromo-1-chloroethane	83	1.667 ¹⁶ / ₄
Ethylene chloride	83	1.256	1.4443
Trichloroethylene	90	1.440 ¹⁵ / ₀	1.4782
Methylene bromide	98	2.498 ¹⁵ / ₄
Propylene chloride	98	1.166 ¹⁴ / ₄	1.4388
1-Bromo-2-chloroethane	107	1.689 ¹⁹ / ₄
Ethylidene bromide	112	2.100 ¹⁷ / ₄	1.5128
1,1,2-Trichloroethane	114	1.457 ¹⁰ / ₄	1.4711
Tetrachloroethylene	121	1.631 ⁹ / ₄	1.5055
Trimethylene chloride	125	1.190 ¹⁸ / ₄
Ethylene bromide	130	2.178	1.5379
2,3-Dibromopropene	140
Propylene bromide	142	1.933	1.5203
Trimethylene chlorobromide	143	1.593 ²⁰ / ₄	1.4708
<i>s</i> -Tetrachloroethane	147	1.614 ⁰ / ₄	1.4942
Isobutylene bromide	149	1.759	1.509
Bromoform	151	2.904 ¹⁸ / ₄	1.589
1,2,3-Trichloropropane	155	1.417
2,3-Dibromobutane	158	1.830
Pentachloroethane	161	1.693 ¹⁰ / ₄	1.504
1,2-Dibromobutane	165	1.820 ²⁹ / ₀
Trimethylene bromide	165	1.973 ¹⁷ / ₄	1.523
1,3-Dibromobutane	174	1.807	1.507
Methylene iodide	180d.	3.285 ¹⁵ / ₄	1.7425/15
<i>s</i> -Tetrabromoethane	200d.	2.971 ¹⁷ / ₄	1.638
Benzal chloride	212	1.295 ¹⁶ / ₄	1.5515
<i>o</i> -Chlorobenzyl chloride	214
<i>p</i> -Chlorobenzyl chloride	214
1,2,3-Tribromopropane	219	2.436 ²⁹ / ₄	1.584
Benzotrichloride	220	1.380 ¹⁴ / ₄	1.5573
Pentamethylene bromide	221	1.706 ¹⁸ / ₄

HALIDES—POLYHALOGEN DERIVATIVES OF NON-BENZENOID HYDROCARBONS
(SOLIDS)

Name of Compound	M. P.	Derivative
<i>p</i> -Chlorobenzyl chloride	29°	<i>p</i> -Chlorobenzoic acid 242°
Heptachloropropane	29
<i>o</i> -Bromobenzyl bromide	30	<i>o</i> -Bromobenzoic acid 150
<i>p</i> -Bromobenzyl bromide	63
Ethylene iodide	82	Ethylene glycol di- β -naphthyl ether 148
Carbon tetrabromide	92
Iodoform	119	Quinoline addition compound 65
α -Benzene hexachloride	157
<i>s</i> -Tetramethyldichloroethane	160
<i>s</i> -Tetramethyldibromoethane	169
Hexachloroethane	187
β -Benzene hexachloride	310

TABLE XXXIV
HYDROCARBONS—AROMATIC (LIQUIDS)

Name	B. P.	Sp. Gr.	Nitration Product		Aroyl- benzoic Acid	Picrate
			Position	M. P.		
Benzene.....	80°	0.874	1, 3	89°	127°	84°
Toluene.....	111	0.881 ⁴ / ₄	2, 4	70	137	88
Ethylbenzene.....	135	0.876 ¹⁹ / ₄	2, 4, 6	37	122	96
<i>p</i> -Xylene.....	137	0.866 ¹⁴ / ₄	2, 3, 5	137	132	90
<i>m</i> -Xylene.....	139	0.871 ¹² / ₄	2, 4	83	126	91
<i>o</i> -Xylene.....	142	0.890 ⁴ / ₄	4, 5	71	178	88
Isopropylbenzene (Cu- mene).....	153	0.875 ⁴ / ₄	2, 4, 6	109	133
<i>n</i> -Propylbenzene.....	158	0.861	125	103
Mesitylene.....	164	0.869 ¹⁰ / ₄	2, 4	86	211	97
Pseudocumene.....	168	0.895	3, 5, 6	185	97
<i>p</i> -Cymene.....	175	0.857	2, 6	54	123
<i>m</i> -Diethylbenzene.....	182	0.860	2, 4, 6	62	114
<i>n</i> -Butylbenzene.....	182	0.862	97
Isodurene.....	195	4, 6	157	213
<i>n</i> -Amylbenzene.....	202	0.866 ¹⁶ / ₁₆
Prehnitene.....	204	0.901 ²⁰ / ₄	5, 6	176
Tetralin.....	206	0.971	5, 7	95	153
1,3,5-Triethylbenzene.....	218	0.863	2, 4, 6	108	129
Cyclohexylbenzene.....	237	0.955	4	58
α -Methylnaphthalene.....	240	1.001 ¹⁹ / ₄	4	71	169	141
1,1-Diphenylethane.....	270	1.003 ²⁰ / ₀

HYDROCARBONS—AROMATIC (SOLIDS)

Name	M. P.	Nitration Product		Aroyl- benzoic Acid	Picrate
		Position	M. P.		
Diphenylmethane.....	26°	2, 4, 2', 4'	172°
β -Methylnaphthalene.....	32	1	81	116°
Pentamethylbenzene.....	51	6	154	131
Dibenzyl.....	52	4, 4'	180
Biphenyl.....	70	4, 4'	233	224°
Durene.....	79	3, 6	205	263
Naphthalene.....	80	1	61	172	149
<i>m</i> -Diphenylbenzene.....	85
Triphenylmethane.....	92	4, 4', 4''	206
Acenaphthene.....	95	5	101	198	161
Retene.....	98	124
Phenanthrene.....	100	144
Fluorene.....	115	2, 7	199	227	84
α,α' -Binaphthyl.....	160	145
Hexamethylbenzene.....	162	176	170
β,β' -Binaphthyl.....	188	184
<i>s</i> -Tetraphenylethane.....	211	4, 4, 4, 4	143
Terphenyl.....	213
Anthracene.....	216	138

TABLE XXXV

HYDROCARBONS—PARAFFINS AND CYCLOPARAFFINS

Name	B. P.	Sp. Gr.	n_D^{20}
Neopentane.....	9°	0.613 $\frac{0}{0}$	1.3513 (0°)
Isopentane.....	31	0.613 $\frac{14}{4}$	1.355
Pentane.....	36	0.631	1.3570
Cyclopentane.....	50	0.750	1.4093
<i>n</i> -Hexane.....	68	0.660	1.3754
Cyclohexane.....	80	0.790	1.4263
<i>n</i> -Heptane.....	98	0.684	1.385
2,2,4-Trimethylpentane.....	99	0.692 $\frac{20}{4}$	1.3916
Methylcyclohexane.....	100	0.769	1.4235
<i>n</i> -Octane.....	125	0.703	1.3890
<i>n</i> -Nonane.....	149	0.717	1.405
Diisooamyl.....	158	0.735 $\frac{10}{4}$	1.408
<i>p</i> -Menthane.....	169	0.796 $\frac{15}{4}$	1.437
<i>n</i> -Decane.....	173	0.730	1.415
Decalin (<i>trans</i>).....	185	0.870	1.4697
Decalin (<i>cis</i>).....	194	0.896	1.4811
<i>n</i> -Undecane.....	194	0.745 $\frac{15}{4}$	1.4184
<i>n</i> -Dodecane.....	215	0.755 $\frac{15}{4}$	1.4209

TABLE XXXVI
HYDROCARBONS—UNSATURATED

Name	B. P.	M. P.	Sp. Gr.	n_D	Derivative M. P.
3-Methyl-1-butene....	21°		0.660 ¹⁵ / ₁₆
2-Pentene.....	36		0.651	1.3789
Trimethylethylene....	38		0.668 ¹³ / ₄	1.3855
1-Pentyne.....	40		0.688	1.4079	Mercuride.... 118°
Cyclopentadiene.....	42		0.805 ¹⁹ / ₄	1.4470
Cyclopentene.....	46		0.774 ¹⁸ / ₄	1.4218
Diallyl.....	59		0.690	1.4010
1-Hexyne.....	70		0.712	Mercuride.... 99
Tetramethylethylene..	72		0.728 ⁹ / ₄
Cyclohexene.....	84		0.809	1.4492	Adipic acid... 152
1-Heptyne.....	100		0.750 ¹⁹ / ₄	1.418	Mercuride.... 61
Diisobutylene.....	101		0.715 ²⁰ / ₄	1.4082
Δ^3 -Tetrahydrotoluene.	103		0.799	1.4430	β -Methyladipic acid..... 93
Δ^2 -Tetrahydrotoluene.	105		0.800	1.4426	α -Methyladipic acid..... 64
Δ^1 -Tetrahydrotoluene.	111		0.809	1.4496	Nitrosochloride 97
Phenylacetylene.....	140		0.930	1.5524	Mercuride.... 125
Styrene.....	146		0.925	1.5485	Dibromide.... 73
<i>l</i> -Bornylene.....	146	113°			
<i>d</i> - or <i>l</i> -Pinene.....	156		0.858	1.4653	Dibromide.... 164
Allylbenzene.....	157		0.893		
<i>l</i> -Camphene.....	160	42	0.822	1.4621	Dibromide.... 89
Limonene.....	176		0.846 ¹⁸ / ₄	1.4727	Tetrabromide. 104
Sylvestrene.....	176		0.851 ¹⁶ / ₄	1.4774	Tetrabromide. 135
Propenylbenzene.....	177		0.914 ¹⁵ / ₁₅	1.5143
Hydrindene.....	177		0.965 ²⁰ / ₄	1.5381
Indene.....	180		0.963 ¹⁶ / ₄	1.5710	Picrate..... 98
Dipentene.....	181		0.854 ¹⁶ / ₄	1.4730	Tetrabromide. 124
Dihydronaphthalene..	212	15	0.998	1.5740
1,1-Diphenylethylene.	277	8	1.038 ¹⁴ / ₄	1.5967
Stilbene.....	306	125	0.970 ¹²⁵ / ₁₅	Dibromide.... 237
1,4-Diphenylbutadiene (<i>trans</i>).....	350	148		
1,4-Diphenylbutadiene (<i>cis</i>).....		70		
1,1,2-Triphenylethylene.....		73		

TABLES OF DERIVATIVES

TABLE XXXVII

KETONES (Liquids)

Name of Compound	B. P.	Derivatives			
		Oxime	Semi-carbazone	Phenyl-hydrazone	2,4-Dinitrophenylhydrazone
Acetone.....	56°	59°	187°	42°	126°
Ethyl methyl ketone.....	80		146		117
Methyl vinyl ketone.....	80		141		
Biacetyl.....	88	$\left\{ \begin{array}{c} 74 \\ \text{(mono)} \\ 245(\text{di}) \end{array} \right\}$	278	245	315
Isopropyl methyl ketone..	94		113		117
Methyl <i>n</i> -propyl ketone...	102	58	110		144
Diethyl ketone.....	102	69	139		156
Pinacolone.....	106	74	157		125
Isobutyl methyl ketone...	119	58	135		95
Chloroacetone.....	119		164d.		
α,α -Dichloroacetone.....	120		163		
Diisopropyl ketone.....	125	34	160		95
<i>n</i> -Butyl methyl ketone....	129	49	122		106
Mesityl oxide.....	130	49	164	142	203
Cyclopentanone.....	131	56	205	50	142
Bromoacetone.....	136	36			
Acetylacetone.....	139	149			$\left\{ \begin{array}{c} \text{(mono)} \\ 122 \\ \text{(di)} 209 \end{array} \right\}$
Di- <i>n</i> -propyl ketone.....	145		133		75
Acetoin.....	145		185	243d.	315
Hydroxyacetone (Acetol)..	146	71	196	103	129
<i>n</i> -Amyl methyl ketone....	151		127	207	89
Cyclohexanone.....	155	90	166	77	162
Di- <i>sec</i> -butyl ketone.....	162		84		
2-Methylcyclohexanone...	163	43	195		137
Diacetone alcohol.....	164	57			203
Diisobutyl ketone.....	168	210	121		92
3-Methylcyclohexanone...	169		180		155
4-Methylcyclohexanone...	169	37	199		130
<i>n</i> -Hexyl methyl ketone....	172		122		58
Methyl cyclohexyl ketone.	180	60	177		140
Cycloheptanone.....	181	23	163		148
Di- <i>n</i> -butyl ketone.....	187		90		

TABLE XXXVII—*Continued*KETONES (LIQUIDS)—*Continued*

Name of Compound	B. P.	Derivatives			
		Oxime	Semi-carbazone	Phenyl-hydrazone	2,4-Dinitrophenylhydrazone
Acetonylacetone.....	188°	(di) 137°	(di) 220°	(di) 120°	255°
Butyrolin.....	190	99
Phorone.....	198	48	186	112
Acetophenone.....	200	59	198	105	250
β -Thujone.....	202	55	174	114
<i>l</i> -Menthone.....	207	59	187	53	146
Isophorone.....	214	76	191	68
Methyl 2-thienyl ketone..	214	81	191	95
Benzyl methyl ketone....	216	70	198	87
Methyl <i>o</i> -tolyl ketone....	216	61	206	159
Propiophenone.....	218	53	174	191
Methyl <i>m</i> -tolyl ketone....	220	57	200
Methyl <i>p</i> -tolyl ketone....	222	86	205	94	260
Isobutyrophenone.....	222	{ 61 94	181	73	163
Pulegone.....	224	174	142
Isovalerophenone.....	225	74	210	240
Carvone.....	225	72	142	106	193
Di- <i>n</i> -amyl ketone.....	226
Benzyl ethyl ketone.....	226	135
Phenyl <i>n</i> -propyl ketone..	230	50	184	200
<i>p</i> -Chloroacetophenone....	232	95	114	231
Methyl β -phenylethyl ketone.....	235	85	142
Acetomesitylene.....	245
2-Aceto- <i>p</i> -cymene.....	250
Dypnone.....	345	{ <i>syn</i> 134 <i>anti</i> 78	151

TABLE XXXVII—Continued

KETONES (SOLIDS)

Name of Compound	M. P.	B. P.	Derivatives			
			Oxime	Semicarbazone	Phenylhydrazone	2,4-Dinitrophenylhydrazone
Benzyl methyl ketone....	27°	216°	70°	198°	87°
3-Hydroxyacetophenone....	28	218	117	210	110
Phorone.....	28	198	48	186
Dibenzyl ketone.....	34	330	125	146	120	100°
<i>p</i> -Methoxyacetophenone....	38	258	87	198	142	220
Benzalacetone.....	41	262	115	187	157	223
1-Indanone.....	42	242	146	233	135	258
α,α' -Dichloroacetone....	45	173	120
Thymoquinone.....	45	232	162	202	93*	180*
Benzophenone.....	48	305	141	164	137	239
ω -Bromoacetophenone....	50	{ 88 97 }	146
(Phenacyl bromide)						
<i>p</i> -Bromoacetophenone....	51	255	128	126	230
Methyl β -naphthyl ketone	53	300	145	237	176	262
Phenyl <i>p</i> -tolyl ketone....	54	326	{ 154 136 }	122	109	200
ω -Chloroacetophenone....	59	244	89	156	212
(Phenacyl chloride)						
Desoxybenzoin.....	60	320	98	148	116	204
Benzalacetophenone.....	62	348	{ 73 75 }	{ 168 180 }	120	245
<i>p</i> -Methoxybenzophenone....	62	355	{ 116 138 }	{ 132 90 }
<i>p</i> -Toluquinone.....	68	134	179	130*	128*
Laurone.....	69	40
<i>d</i> - α -Bromocamphor.....	76	274
<i>m</i> -Nitroacetophenone....	81	202	132	257	128
Fluorenone.....	83	341	195	151	283
Di- <i>p</i> -tolyl ketone.....	92	334	163
Benzil.....	95	347	{ 137 (mono) 237(di)	{ 182 (mono) 244(di)	{ 225 (di)	189
<i>p</i> -Bromophenacyl bromide	109	115

TABLE XXXVII—Continued

KETONES (SOLIDS)—Continued

Name of Compound	M. P.	B. P.	Derivatives			
			Oxime	Semi-carbazone	Phenyl-hydrazone	2,4-Dinitrophenyl-hydrazone
Dibenzalacetone.....	112°	144°	190°	180°
Benzoquinone.....	115	240d.	243	152°*	231*
β -Naphthoquinone...	120	169	184	138*
α -Naphthoquinone...	125	207	247	206*	278*
<i>p</i> -Phenylphenacyl bromide.....	125
Vanillidineacetone...	130	128	230
Benzoin.....	133	343°	151	206d.	106	245
Methone(5,5-Dimethyl-dihydroresorcinol).....	149	{ (mono) 115 (di)(anhyd) 176 }
Benzanthrone.....	170
Quinhydrone.....	171
Xanthone.....	173	350	161	152
Gallacetophenone.....	173	163	225
<i>dl</i> -Camphor.....	178	205	118	164
<i>d</i> -Camphor.....	179	205	118	237	233	177
β -Methylantraquinone.....	179
Camphorquinone....	198	{ 170 (mono) 140(di) }	{ 236 147 }	170*	{ 36 }* { 190 }
Phenanthraquinone..	207	360	{ 158 (mono) 202(di) }	220d.	165*	313d.
Phloroacetophenone..	219
Anthraquinone.....	286	224	183*
Alizarin.....	289
Chloranil.....	290	220

* These melting points are those of the addition compounds of the quinones and substituted hydrazines. The products are not true hydrazones.

TABLE XXXVIII

MERCAPTANS

Mercaptan	B. P.	M. P.	2,4-Dinitro- phenyl Thio Ether
Methyl.....	6°	128°
Ethyl.....	36	115
Isopropyl.....	56	94
<i>n</i> -Propyl.....	67	81
Isobutyl.....	88	76
<i>n</i> -Butyl.....	97	66
<i>sec</i> -Amyl.....	112
Isoamyl.....	117	59
<i>n</i> -Amyl.....	126	80
<i>n</i> -Hexyl.....	151	74
Thienyl.....	166	119
Phenyl (Thiophenol).....	169	121
<i>n</i> -Heptyl.....	176	82
Benzyl.....	194	130
<i>p</i> -Tolyl (<i>p</i> -Thiocresol).....	195	43°	103
<i>n</i> -Octyl.....	199	78
<i>n</i> -Nonyl.....	220	86
Cetyl.....	170 (3 mm.)	50	91
Biphenyl.....	111	146

TABLE XXXIX
NITRILES (LIQUIDS)

Name of Compound	B. P.	Semicarbazone of Alkyl Phenyl Ketone	Alkyl 2,4,6-Trihydroxyphenyl Ketone	α -Iminoalkyl-mercaptoacetic Acid Hydrochloride
Acrylonitrile.....	78°			
Acetonitrile.....	81	199°	218°	114°
Propionitrile.....	97	174	175	124
Isobutyronitrile.....	108			
<i>n</i> -Butyronitrile.....	118	184	181	135
β -Butenitrile (Allyl cyanide).....	118			
α -Hydroxyisobutyronitrile.....	120			
Methoxyacetoneitrile.....	120			
Isovaleronitrile.....	130			133
<i>n</i> -Valeronitrile.....	141	157	149 (Hydrate 88)	137
Furonitrile.....	146			
Isocaproitrile.....	155	146	122 (Hydrate 104)	128
<i>n</i> -Capronitrile.....	164	128	121 (Hydrate 96)	136
Mandelonitrile.....	170d.			
Lactonitrile.....	182d.			
Oenanthonitrile.....	183			133
Benzonitrile.....	191			124
γ -Chlorobutyronitrile.....	197			
Caprylonitrile.....	200			134
<i>o</i> -Tolunitrile.....	205			
Ethyl cyanoacetate.....	207			
<i>m</i> -Tolunitrile.....	212			168
<i>p</i> -Tolunitrile.....	217			181
Malononitrile.....	219			
β -Hydroxypropionitrile.....	221			
Phenylacetoneitrile.....	234			144
Cinnamonitrile.....	254			
Glutaronitrile.....	286			

NITRILES (SOLIDS)

Name of Compound	M. P.	B. P.	Name of Compound	M. P.	B. P.
α -Naphthonitrile.....	35°	299°	<i>p</i> -Nitrophenylacetoneitrile.....	116°
<i>p</i> -Tolunitrile.....	38	217	<i>m</i> -Nitrobenzonitrile.....	118
Succinonitrile.....	54	267d.	Methyleneaminoacetoneitrile.....	129
β -Naphthonitrile.....	66	306	<i>p</i> -Nitrobenzonitrile.....	147
Cyanoacetic acid.....	66	165d.			
<i>p</i> -Chlorobenzonitrile.....	92			
<i>p</i> -Bromobenzonitrile.....	112			

TABLE XL
NITRO COMPOUNDS (LIQUIDS)

Name of Compound	B. P.	Acyl Derivatives of the Amine		Other Derivatives
		Benzene-sulfonamide	Benzamide	
Nitromethane.....	101°	30°	80°
Chloropicrin.....	113
Nitroethane.....	114	58	71
2-Nitropropane.....	120	26	Amine·HCl..... 140°
Tetranitromethane.....	126
1-Nitropropane.....	130	36	84	Amine·HCl..... 157
1-Nitrobutane.....	152
Nitrobenzene.....	209	112	160	<i>m</i> -Dinitrobenzene..... 90
<i>o</i> -Nitrotoluene.....	224	124	143	2,4-Dinitrotoluene..... 70
<i>o</i> -Nitroethylbenzene.....	224	147
2,6-Dimethylnitrobenzene.....	225	2-Nitroisophthalic acid 300
Phenylnitromethane.....	226d.	88	105
<i>m</i> -Nitrotoluene.....	231	95	125	CHCl ₃ addn. cpd..... 100
2,5-Dimethylnitrobenzene.....	234	138	140	Trinitro- <i>p</i> -xylene..... 137
2,4-Dimethylnitrobenzene.....	238	128	192	1,3-Dimethyl-4,6-dinitrobenzene..... 93
<i>p</i> -Nitroethylbenzene.....	241	151	Trinitroethylbenzene..... 37
2,3-Dimethylnitrobenzene.....	250
β -Nitrostyrene.....	260d.
2-Nitrocymene.....	264	102	2,6-Dinitrocymene..... 54
<i>o</i> -Nitroanisole.....	265	89	2,4,6-Trinitroanisole..... 68
<i>o</i> -Nitrophenetole.....	268	102	2,4-Dinitrophenetole..... 86

NITRO COMPOUNDS (SOLIDS)

Name of Compound	M. P.	B. P.	Acyl Derivatives of the Amine		Special Derivatives
			Benzene-sulfonamide	Benzamide	
Tribromonitromethane.....	10°
Tetranitromethane.....	13	126°
Trinitromethane.....	15
Nitroform.....	15	NH ₄ salt..... 200° d.
<i>m</i> -Nitrotoluene.....	16	231	95°	125°	CHCl ₃ addn. cpd..... 100
<i>m</i> -Nitrobenzyl alcohol.....	27	Benzoate..... 94
3,4-Dimethylnitrobenzene.....	29	258

TABLE XL—Continued
NITRO COMPOUNDS (SOLIDS)—Continued

Name of Compound	M. P.	B. P.	Acyl Derivatives of the Amine		Special Derivatives
			Benzene-sulfonamide	Benzamide	
<i>o</i> -Chloronitrobenzene	32°	246°	129°	99°	2,4-Dinitrochlorobenzene..... 50°
2-Nitrobiphenyl.....	33				
<i>m</i> -Nitroanisole.....	38	258			
<i>o</i> -Bromonitrobenzene	43	261		116	2,4-Dinitrobromobenzene..... 72
<i>m</i> -Chloronitrobenzene	44	235	121	120	3,4-Dinitrochlorobenzene..... 72
Nitromesitylene.....	44	225		204	Dinitromesitylene.... 86
<i>o</i> -Nitrobenzyl chloride	48				
<i>o</i> -Nitroiodobenzene.....	49				
2,4-Dinitrochlorobenzene.....	52*	315d.		178	2,4-Dinitrophenol.... 114
2,5-Dichloronitrobenzene.....	54			120	2,5-Dichloro-1,3-dinitrobenzene..... 104
<i>p</i> -Nitroanisole.....	54	258	95	154	2,4-Dinitroanisole.... 89
<i>m</i> -Bromonitrobenzene	54	257		136	3,4-Dinitrobromobenzene..... 59
<i>p</i> -Nitrotoluene.....	54	238	120	158	2,4-Dinitrotoluene.... 70
β -Nitrostyrene.....	58	260d.			
<i>p</i> -Nitrophenetole.....	60	283	143	173	2,4-Dinitrophenetole.. 86
α -Nitronaphthalene..	61	304	167	130	
<i>m</i> -Nitrobenzyl chloride.....	65				
2,6-Dinitrotoluene.....	66				
2,4,6-Trinitroanisole..	68				Picric acid..... 122
2,4-Dinitrotoluene....	70				2,4,6-Trinitrotoluene.. 82
<i>p</i> -Nitrobenzyl chloride.....	71				<i>p</i> -Toluidine..... 45
2,4-Dinitrobromobenzene.....	72				2,4-Dinitrophenol.... 114
<i>o</i> -Nitrobenzyl alcohol	74	270d.			Acetate..... 35
3,5-Dimethylnitrobenzene.....	75	273			
2,4,6-Trinitrophenetole.....	78				
β -Nitronaphthalene....	78		136	162	Picric acid..... 122
2,4,6-Trinitrotoluene	82				2,4,6-Trinitrobenzoic acid..... 220
<i>p</i> -Chloronitrobenzene	83	242	121	192	<i>p</i> -Nitrophenol..... 114
Picryl chloride.....	83		211		Picric acid..... 122
2,4-Dinitroanisole....	89				2,4-Dinitrophenol.... 114
<i>m</i> -Dinitrobenzene.....	90	302	194	240	<i>m</i> -Nitroaniline..... 114
3,5-Dinitrotoluene....	92				
<i>p</i> -Nitrobenzyl alcohol	93				Acetate..... 78

* Metastable forms melting at 27° and 43° are also reported.

TABLE XL—Continued

NITRO COMPOUNDS (SOLIDS)—Continued

Name of Compound	M. P.	B. P.	Acyl Derivatives of the Amine		Special Derivatives
			Benzene-sulfonamide	Benzamide	
2,4-Dimethyl-1,3-dinitrobenzene.....	93°				2,4-Dimethyl-1,3,5-trinitrobenzene..... 125°
<i>p</i> -Nitrobenzyl bromide.....	99				
4-Nitrobiphenyl.....	113			230°	
<i>o</i> -Dinitrobenzene.....	118	319°	186°	301	<i>o</i> -Nitroaniline..... 71
1,3,5-Trinitrobenzene.....	122				Naphthalene addn. cpd. 153
<i>p</i> -Bromonitrobenzene.....	126	259	134	204	<i>p</i> -Nitrophenol..... 114
<i>p,p'</i> -Dinitrophenyl ether.....	143				
1,8-Dinitronaphthalene.....	170				1,3,8-Trinitronaphthalene..... 218
<i>p</i> -Nitroiodobenzene.....	171			210	
<i>p</i> -Dinitrobenzene.....	172	299	247	300	<i>p</i> -Nitrophenol..... 114
1,5-Dinitronaphthalene.....	214				1,4,5-Trinitronaphthalene..... 154

TABLE XLI

NITROSO, AZOXY, AZO, AND HYDRAZO COMPOUNDS

Compound	M. P.	Compound	M. P.
<i>Nitroso Compounds:</i>		<i>Azoxy Compounds—Continued</i>	
<i>N</i> -Nitrosodiphenylamine.....	66°	<i>p,p'</i> -Dichloroazoxybenzene.....	154°
Nitrosobenzene.....	68		
<i>p</i> -Nitroso- <i>N,N</i> -diethyl-aniline.....	84	<i>Azo Compounds:</i>	
<i>p</i> -Nitroso- <i>N,N</i> -dimethyl-aniline.....	87	<i>o</i> -Azotoluene.....	55
1-Nitroso-2-naphthol.....	109	Azobenzene.....	68
<i>p</i> -Nitroso- <i>N</i> -methylaniline.....	116	Benzeneazodiphenylamine.....	96
<i>p</i> -Nitrosophenol.....	125d.	<i>p</i> -Dimethylaminoazobenzene.....	117
<i>p</i> -Nitrosodiphenylamine.....	144	<i>p</i> -Aminoazobenzene.....	125
2-Nitroso-1-naphthol.....	152d.	Benzeneazo- <i>o</i> -cresol.....	128
Nitrosothymol.....	162	1-Benzeneazo-2-naphthol.....	131
4-Nitroso-1-naphthol.....	194d.	<i>o</i> -Azophenetole.....	131
<i>Azoxy Compounds:</i>		<i>p</i> -Azotoluene.....	144
Azoxybenzene.....	36	<i>p</i> -Hydroxyazobenzene.....	152
<i>o</i> -Azoxytoluene.....	59	<i>p</i> -Azophenetole.....	160
<i>p</i> -Azoxytoluene.....	75	2,2'-Azonaphthalene.....	208
		<i>Hydrazo Compounds:</i>	
		Hydrazobenzene.....	130
		<i>o</i> -Hydrazotoluene.....	161

TABLE XLII
PHENOLS (LIQUIDS)

Name of Compound	B. P.	M. P.	Derivatives		
			α -Naphthyl-urethan	Bromo Derivatives	Aryloxy-acetic Acid
<i>o</i> -Chlorophenol.....	175°	7°	120°	145°
Phenol.....	180	42	133	Tribromo... 95°	99
<i>o</i> -Cresol.....	190	31	142	Dibromo... 56	152
<i>o</i> -Bromophenol.....	195	129	Tribromo... 95	143
<i>p</i> -Cresol.....	202	36	146	Dibromo... 49	136
<i>m</i> -Cresol.....	202	3	128	Tribromo... 84	103
Guaiacol.....	205	28	118	Tribromo... 116	121
2,4-Dichlorophenol.....	209	43	Bromo... 68	138
<i>m</i> -Chlorophenol.....	214	28	158	110
<i>p</i> -Chlorophenol.....	217	37	166	156
<i>m</i> -Bromophenol.....	236	32	108
Carvacrol.....	237	0	116	Bromo... 46	151
2,4-Dibromophenol.....	238	36	Tribromo... 95
Resorcinol monomethyl ether	243	129	Tribromo... 104	118
Eugenol.....	250	122	Tetrabromo... 118	80
Isoeugenol.....	267	150	Dibromo... 94	94

PHENOLS (SOLIDS)

Name of Compound	M. P.	Derivatives		
		α -Naphthyl-urethan	Bromo Derivatives	Esters
2,4-Dimethylphenol.....	26°	135°	Benzoate..... 33°
Guaiacol.....	28	118	Tribromo... 116	Benzoate..... 57
<i>o</i> -Cresol.....	31	142	Dibromo... 56	3,5-Dinitrobenzoate... 133
<i>m</i> -Bromophenol.....	32
<i>p</i> -Cresol.....	36	146	Tetrabromo... 108	Benzoate..... 71
2,4-Dibromophenol.....	36	Tribromo... 95	Benzoate..... 97
<i>p</i> -Chlorophenol.....	37	166	Benzoate..... 93
<i>m</i> -Iodophenol.....	40
Phenol.....	42	133	Tribromo... 95	Benzoate..... 68
2,4-Dichlorophenol.....	43	Bromo... 68	Benzoate..... 97
<i>o</i> -Iodophenol.....	43
<i>o</i> -Nitrophenol.....	45	113	4,6-Dibromo 117	3,5-Dinitrobenzoate... 142
2,6-Dimethylphenol.....	49	176	Bromo..... 79
Thymol.....	50	160	Bromo..... 55	Benzoate..... 32
<i>o</i> -Cyclohexylphenol.....	53
Hydroquinone monomethyl ether.....	53
2-Hydroxy-3,5-dibromotoluene.....	57
Orcinol (hydrated).....	58	160	Tribromo... 104	Dibenzoate... 88
<i>o</i> -Phenylphenol.....	58	Dinitro..... 207
4-Chlorothymol.....	59

TABLE XLII—Continued

PHENOLS (SOLIDS)—Continued

Name of Compound	M. P.	Derivatives		
		α -Naphthylurethan	Bromo Derivatives	Esters
1,2-Dihydroxynaphthalene	60°	Diacetate.... 106°
<i>p</i> -Bromophenol.....	63	169°	Tribromo... 95°	Benzoate.... 102
3,4-Dimethylphenol.....	63	142	Tribromo... 171	Benzoate.... 58
2-Chloro-5-hydroxytoluene	66	154	Benzoate.... 86
2,4,6-Trichlorophenol.....	67	Benzoate.... 70
3,5-Dimethylphenol.....	68	Tribromo... 166	3,5-Dinitrobenzoate... 195
2,4,6-Trimethylphenol.....	69	Dibromo... 158
4- <i>n</i> -Hexylresorcinol.....	69
Pseudocumenol.....	71	Bromo..... 35	Benzoate.... 63
2,5-Dimethylphenol.....	74	173	Tribromo... 178	Benzoate.... 61
<i>p</i> -Benzylphenol.....	84	Benzoate.... 87
2-Hydroxy-3,5-dinitro- toluene.....	86	Benzoate.... 132
α -Naphthol.....	91	152	2,4-Dibromo 105	Acetate.... 46
<i>p</i> -Iodophenol.....	94	Benzoate.... 119
<i>p</i> - <i>tert</i> -Butylphenol.....	95	Bromo..... 50	Benzoate.... 83
2,4,6-Tribromophenol.....	95	153	Tetrabromo 120	Acetate.... 82
<i>p</i> - <i>tert</i> -Amylphenol.....	96
<i>m</i> -Nitrophenol.....	97	167	Dibromo... 91	Benzoate.... 95
Catechol.....	104	Tetrabromo 192	Diacetate.... 63
Chlorohydroquinone.....	106	Diacetate.... 72
Orcinol.....	107	160	Tribromo... 104	Dibenzoate... 88
Resorcinol.....	110	4,6-Dibromo 112	Dibenzoate... 117
3-Hydroxy-2,4,6-trinitro- toluene.....	110	Acetate.... 135
Bromohydroquinone.....	110	Dibromo... 186	Diacetate.... 72
<i>p</i> -Nitrophenol.....	114	151	2,6-Dibromo 142	Acetate.... 81
2,4-Dinitrophenol.....	114	6-Bromo... 118	Acetate.... 72
<i>p</i> -Hydroxybenzaldehyde.....	115	3,5-Dibromo 181
Hydroquinone monoben- zyl ether.....	122
Picric acid.....	122	Acetate.... 76
β -Naphthol.....	122	157	Bromo..... 84	Acetate.... 70
Toluidohydroquinone.....	124	Diacetate.... 52
<i>p</i> -Cyclohexylphenol.....	132
Pyrogallol.....	133	Dibromo... 158	Triacetate.... 165
2,4-Dinitronaphthol.....	138	Benzoate.... 174
1,8-Dihydroxynaphthalene	140	Diacetate.... 148
<i>p</i> -Phenylphenol.....	165	Acetate.... 89
Hydroquinone.....	169	Dibromo... 186	Diacetate.... 123
Gallacetophenone.....	173
1,4-Dihydroxynaphthalene	176	Diacetate.... 128
Carbostyryl.....	200
Tetrabromo- <i>o</i> -cresol.....	210	Acetate.... 154
Phloroglucinol.....	218	Tribromo... 151	Triacetate.... 105
Di- β -naphthol.....	218
1,5-Dihydroxynaphthalene	258	Diacetate.... 160
Phenolphthalein.....	261	Diacetate.... 146
<i>p,p'</i> -Dihydroxybiphenyl.....	272	Diacetate.... 160
Di- α -naphthol.....	300

TABLE XLIII
SULFONAMIDES (Solids)

Sulfonamide	M. P.	Sulfonamide	M.P.
3-Methyl-1-butane-.....	3°	4,6-Dichloro-2,5-dimethylbenzene-.....	150°
2-Methyl-1-propane-.....	16	<i>o</i> -Toluene-.....	153
1-Butane-.....	45	Benzene-.....	153
1-Propane-.....	52	<i>o</i> -Aminobenzene-.....	153
Ethane-.....	58	<i>m</i> -Bromobenzene-.....	154
2-Propane-.....	60	2-Iodo-1-naphthalene-.....	154
4-Isopropyl-2-methylbenzene-.....	73	2,6-Dichloro-4-methylbenzene-.....	155
1-Heptane-.....	75	2,3-Dichloro-5-methylbenzene-.....	158
3-Ethylbenzene-.....	86	<i>m</i> -Nitrobenzyl-.....	159
Methane-.....	90	3-Chloro-2-methyl-5-nitrobenzene-.....	161
2,6-Dimethylbenzene-.....	96	<i>p</i> -Aminobenzene-.....	163
2-Ethylbenzene-.....	100	4-Chloro-2-nitrobenzene-.....	164
3-Methyl-4-fluorobenzene-.....	105	3,6-Dichloro-2,5-dimethylbenzene-.....	165
Benzyl-.....	105	<i>m</i> -Nitrobenzene-.....	166
<i>m</i> -Toluene-.....	108	2-Methyl-5-bromobenzene-.....	166
4-Ethylbenzene-.....	109	<i>p</i> -Bromobenzene-.....	166
1-Methyl-6-naphthalene-.....	116	2,3-Dimethylbenzene-.....	167
2-Phenyl-1-ethane-.....	122	2,4-Dimethoxybenzene-.....	167
<i>p</i> -Fluorobenzene-.....	125	5-Chloro-2-methyl-3-nitrobenzene-.....	167
4-Methyl-3-chlorobenzene-.....	128	2-Methyl-4-bromobenzene-.....	168
3-Chloro-4-methoxybenzene-.....	131	2,4-Dichloro-6-methylbenzene-.....	168
<i>d</i> -Camphor-10-.....	132	2,5-Dimethyl-3-nitrobenzene-.....	173
3,5-Dimethylbenzene-.....	135	2-Methyl-4-fluorobenzene-.....	173
3,4-Dichlorobenzene-.....	135	1-Methyl-4-naphthalene-.....	174
<i>d</i> -Camphor-8-.....	137	3,4-Dibromobenzene-.....	175
2,4-Dimethylbenzene-.....	137	2,4-Dichloro-5-methylbenzene-.....	176
<i>p</i> -Toluene-.....	137	2-Chloro-5-methyl-6-nitrobenzene-.....	177
<i>o</i> -Nitrobenzyl-.....	137	<i>p</i> -Nitrobenzene-.....	180
2-Bromo-1-naphthalene-.....	140	2,4-Dichlorobenzene-.....	180
2-Methyl-5-fluorobenzene-.....	141	2,4,5-Trimethylbenzene-.....	181
<i>m</i> -Aminobenzene-.....	142	3-Chloro-2-methyl-6-nitrobenzene-.....	181
2-Methyl-5-chlorobenzene-.....	142	2,5-Dichlorobenzene-.....	181
2,4,6-Trimethylbenzene-.....	142		
<i>d</i> -Camphor-3-.....	143		
3,4-Dimethylbenzene-.....	144		
<i>p</i> -Chlorobenzene-.....	144		
1-Methyl-3-naphthalene-.....	144		
4-Methyl-3-bromobenzene-.....	146		
2,5-Dimethylbenzene-.....	148		
<i>m</i> -Chlorobenzene-.....	148		
1-Naphthalene-.....	150		

TABLE XLIII—*Continued*
SULFONAMIDES (SOLIDS)—*Continued*

Sulfonamide	M.P.	Sulfonamide	M.P.
5-Chloro-4-methyl-2-nitrobenzene.....	181°	2,4-Dichloro-3-methylbenzene.....	203°
5-Chloro-4-methyl-3-nitrobenzene.....	182	<i>p</i> -Iodobenzyl-.....	206
5-Chloro-2-methyl-6-nitrobenzene.....	183	2-Methyl-6-naphthalene-.....	206
1-Chloro-4-naphthalene-.....	185	2,6-Dimethyl-8-naphthalene-...	207
4-Chloro-2,5-dimethylbenzene.....	185	4-Hydroxy-2,6-dimethylbenzene-1,3-di-.....	208
4-Chloro-2-methylbenzene-.....	185	2,4,6-Trichlorobenzene-.....	212d.
<i>o</i> -Bromobenzene-.....	186	1-Nitro-2-naphthalene-.....	214
4-Chloro-1-naphthalene-.....	186	3-Methylbenzene-1,5-di-.....	216
4,5-Dichloro-3-methylbenzene-.....	186	2-Naphthalene-.....	217
2,3-Dichloro-6-methylbenzene-.....	186	2,4,6-Tribromobenzene-.....	220d.
3,5-Dichloro-2-methylbenzene-.....	186	3-Chlorobenzene-1,5-di-.....	224
2-Chloro-4-methylbenzene-.....	186	2-Methylbenzene-1,4-di-.....	224
2,4-Diaminobenzene-1,5-di-.....	187	2,3,4-Trichlorobenzene-.....	226d.
8-Iodo-1-naphthalene-.....	187	3,4-Dichloro-2-methylbenzene-.....	228
<i>o</i> -Chlorobenzene-.....	188	1,3-Benzenedi-.....	229
2,6-Dichloro-3-methylbenzene-.....	188	1-Iodo-5-naphthalene-.....	236
2-Chloro-5-methyl-4-nitrobenzene-.....	188	2-Methylbenzene-1,2-di-.....	237
<i>p</i> -Bromobenzyl-.....	188	2,3-Dichloro-4-methylbenzene-.....	237
1-Methyl-7-naphthalene-.....	189	1,2-Dimethylbenzene-3,5-di-...	239
4-Ethylbenzene-1,3-di-.....	190	4-Methoxybenzene-1,3-di-.....	240
2,4-Dibromobenzene-.....	190	2,7-Naphthalenedi-.....	242
<i>o</i> -Nitrobenzene-.....	191	1,5-Anthraquinonedi-.....	246
4-Methylbenzene-1,3-di-.....	191	2,4-Dimethylbenzene-1,5-di-...	249
2,5-Dimethyl-6-nitrobenzene-.....	192	1,2-Benzenedi-.....	254
1-Bromo-4-naphthalene-.....	193	3-Bromobenzene-1,5-di-.....	256
2,5-Dibromobenzene-.....	194	2-Amino-5-methylbenzene-1,3-di-.....	257
2-Chloro-5-methyl-3-nitrobenzene-.....	196	2-Methylbenzene-1,3-di-.....	260
2,5-Dimethyl-4-nitrobenzene-.....	198	Anthraquinone- β -.....	261
8-Chloro-1-naphthalene-.....	199	1,4-Naphthalenedi-.....	273
<i>p</i> -Nitrobenzyl-.....	200	2,4-Dichlorobenzene-1,5-di-...	276
2,4,5-Trichlorobenzene-.....	>200	1,4-Benzenedi-.....	288
3,4-Dichloro-2,5-dimethylbenzene-.....	201	2,5-Dimethylbenzene-1,3-di-...	295
1-Iodo-4-naphthalene-.....	202	1,6-Naphthalenedi-.....	298
		Biphenyl-4,4'-di-.....	300
		1,5-Naphthalenedi-.....	310
		2,5-Dimethylbenzene-1,4-di-...	310
		1,3,5-Benzenetri-.....	312
		1-Cyano-8-naphthalene-.....	336
		1,8-Anthraquinonedi-.....	340

TABLE XLIV
 SULFONYL CHLORIDES (LIQUIDS)

Sulfonyl Chloride	B. P.	D ₄ ²⁵	Derivatives		
			Acid B.P.	Amide M.P.	Anilide M.P.
Methane.....	60°/21 mm.	1.4490	167°/10 mm.	90°	99°
Ethane.....	70/20 mm.	1.4506	58	58
2-Propane.....	61/9 mm.	1.4522	60	84
1-Propane.....	67/9 mm.	1.4518	136/1 mm.	52	-10
2-Methyl-1-propane..	73/11 mm.	1.4520	16	38
1-Butane.....	75/10 mm.	1.4517	147/0.5 mm.	45
3-Methyl-1-butane...	88/9 mm.	1.4530	3	42
1-Heptane.....	125/9 mm.	75

SULFONYL CHLORIDES (SOLIDS)

Sulfonyl Chloride	M. P.	Derivatives		
		Acid	Amide	Anilide
<i>o</i> -Toluene.....	10°	57°	153°	136°
<i>m</i> -Toluene.....	12	108	96
Benzene.....	14	66	153	110
3,4-Dichlorobenzene..	19	135
2,6-Dichloro-3-methylbenzene..	19	188
2-Methyl-5-chlorobenzene.....	21	142
2,5-Dimethylbenzene.....	25	48	148
<i>o</i> -Chlorobenzene.....	28	188
2-Phenyl-1-ethane.....	33	91	122	77
2,4,5-Trichlorobenzene.....	34
2,4-Dimethylbenzene.....	34	62	137	110
3,4-Dibromobenzene.....	34	175
2-Methyl-5-bromobenzene.....	35	166
<i>p</i> -Fluorobenzene.....	36	125
2,5-Dichlorobenzene.....	38	181	160
2,6-Dimethylbenzene.....	39	98	96
2,4,6-Trichlorobenzene.....	40	212d.
2,3-Dichloro-4-methylbenzene.....	41	237
2,4-Dichloro-6-methylbenzene.....	43	168
2-Chloro-4-methylbenzene.....	46	186

TABLE XLIV—*Continued*
 SULFONYL CHLORIDES (SOLIDS)—*Continued*

Sulfonyl Chloride	M. P.	Derivatives		
		Acid	Amide	Anilide
2,3-Dimethylbenzene.....	47°	167°
2,3-Dichloro-6-methylbenzene.....	49	186
2-Methyl-4-bromobenzene.....	50	168
4-Chloro-2,5-dimethylbenzene.....	50	100	185	155°
<i>o</i> -Bromobenzene.....	51	186
3,4-Dimethylbenzene.....	52	64	144
3,4-Dichloro-2-methylbenzene.....	52	228
2,4-Dichlorobenzene.....	53	180
<i>p</i> -Chlorobenzene.....	53	68	144	104
2-Methyl-4-chlorobenzene.....	53	185
3,5-Dichloro-2-methylbenzene.....	54	186
4-Chloro-2-methylbenzene.....	54	185
2,6-Dichloro-4-methylbenzene.....	56	155
4-Methylbenzene-1,3-di.....	56	191	189
2,4,6-Trimethylbenzene.....	56	77	142	109
2,4-Dichloro-3-methylbenzene.....	59	203
5-Chloro-2-methyl-3-nitrobenzene.....	60	167
4-Methyl-3-bromobenzene.....	60	146
3-Chloro-2-methyl-6-nitrobenzene.....	60	181
2,4,6-Tribromobenzene.....	60	220d.
2,4,5-Trimethylbenzene.....	61	112	181
2,5-Dimethyl-3-nitrobenzene.....	61	200	173	144
3,4-Dichloro-2,5-dimethylbenzene.....	62	201	157
<i>m</i> -Nitrobenzene.....	63	166	126
4-Methyl-3-chlorobenzene.....	63	128
1,3-Benzenedi.....	63	229
2-Chloro-5-methyl-3-nitrobenzene.....	63	196
2,3-Dichloro-5-methylbenzene.....	64	158
3-Chloro-2-methyl-5-nitrobenzene.....	64	161
2,3,4-Trichlorobenzene.....	65	226d.
<i>d</i> -Camphor-10.....	67	193	132	121
1-Naphthalene.....	68	90	150	112
<i>o</i> -Nitrobenzene.....	68	70	191	115
<i>p</i> -Toluene.....	69	92	137	103
5-Chloro-4-methyl-3-nitrobenzene.....	70	182
2,4-Dimethoxybenzene.....	71	192	167
2,5-Dibromobenzene.....	71	194
3,6-Dichloro-2,5-dimethylbenzene.....	71	165	171

TABLE XLIV—Continued

SULFONYL CHLORIDES (SOLIDS)—Continued

Sulfonyl Chloride	M. P.	Derivatives		
		Acid	Amide	Anilide
2,4-Dichloro-5-methylbenzene.....	72°	176°
2,5-Dimethyl-4-nitrobenzene.....	75	140°	198	131°
<i>p</i> -Bromobenzene.....	75	103	166	119
2-Naphthalene.....	76	91	217	132
2,4-Dibromobenzene.....	79	190
1,2-Dimethylbenzene-3,5-di.....	79	239	200
<i>p</i> -Nitrobenzene.....	80	95	180	171
2,5-Dimethylbenzene-1,3-di.....	81	295	174
4,6-Dichloro-2,5-dimethylbenzene.....	81	150	175
1-Methyl-4-naphthalene.....	81	174	158
3-Chloro-4-methoxybenzene.....	82	131
1-Bromo-4-naphthalene.....	83	193
4-Methoxybenzene-1,3-di.....	86	240	209
<i>d</i> -Camphor-3.....	88	143	124
1-Methyl-6-naphthalene.....	88	116
4,5-Dichloro-3-methylbenzene.....	88	186
2-Methylbenzene-1,3-di.....	88	260	162
1,2-Ethanedl.....	91	104
Benzyl.....	92	105	102
2-Chloro-5-methyl-4-nitrobenzene.....	92	188
3,5-Dimethylbenzene.....	94	135	119
3-Methylbenzene-1,5-di.....	95	216	153
4-Chloro-1-naphthalene.....	95	186	143
2-Methylbenzene-1,4-di.....	98	224	178
5-Chloro-4-methyl-2-nitrobenzene.....	99	128	181
3-Bromobenzene-1,5-di.....	100	256
8-Chloro-1-naphthalene.....	101	199
3-Chlorobenzene-1,5-di.....	106	100(d)	224
2,5-Dimethyl-6-nitrobenzene.....	110	145	192	182
2-Iodo-1-naphthalene.....	110	154
4-Methylbenzene-1,2-di.....	111	237	190
1-Iodo-5-naphthalene.....	113	236
2,5-Dichlorobenzene-1,3-di.....	114	217
8-Iodo-1-naphthalene.....	115	187	140
4-Hydroxy-2,6-dimethylbenzene-1,3-di.....	119	208	207
1-Iodo-4-naphthalene.....	121	202	133

TABLE XLIV—*Continued*
 SULFONYL CHLORIDES (SOLIDS)—*Continued*

Sulfonyl Chloride	M. P.	Derivatives		
		Acid	Amide	Anilide
1-Nitro-2-naphthalene-.....	121°	105°	214°	202°
2-Chloro-5-methyl-6-nitrobenzene-.....	122	177
1,7-Naphthalenedi-.....	122
2,4-Dichlorobenzene-1,5-di-.....	123	276
1-Methyl-7-naphthalene-.....	123	189
Diphenylmethane-4,4'-di-.....	124	59	178
1-Methyl-3-naphthalene-.....	125	144
1,6-Naphthalenedi-.....	128	125	298
2,4-Dimethylbenzene-1,5-di-.....	129	249	196
1,3-Naphthalenedi-.....	138
d-Camphor-8-.....	138	137
1,4-Benzenedi-.....	139	288
1,2-Benzenedi-.....	143	254	241
1,3,5-Naphthalenetri-.....	146
5-Chloro-2-methyl-6-nitrobenzene-.....	154	183
1,4,5-Naphthalenetri-.....	156
2-Amino-5-methylbenzene-1,3-di-.....	156	257	192
2,7-Naphthalenedi-.....	162	242
2,5-Dimethylbenzene-1,4-di-.....	164	310	223
1,4-Naphthalenedi-.....	166	273	179
2-Chloro-7-anthraquinone-.....	176
1,5-Naphthalenedi-.....	183	245	310	249
2,7-Anthraquinonedi-.....	186	192
1,3,5-Benzenetri-.....	187	100d.	312	237
1,3,6-Naphthalenetri-.....	193
Anthraquinone-β-.....	197	261	193
1,6-Anthraquinonedi-.....	198	217	227d.
2,3,6-Naphthalenetri-.....	200
2-Chloro-6-anthraquinone-.....	202
Biphenyl-4,4'-di-.....	203	72	300
Anthraquinone-α-.....	214	218	216
1,8-Anthraquinonedi-.....	223	294	340	238
2,6-Naphthalenedi-.....	225
1,7-Anthraquinonedi-.....	232	120	238
2,6-Anthraquinonedi-.....	250	321
1,5-Anthraquinonedi-.....	265d.	310d.	246	270d.
2,4-Diaminobenzene-1,5-di-.....	275	187	236
1,3,5,7-Naphthalenetetra-.....	310

TABLE XLV
MISCELLANEOUS LIQUIDS

This table gives boiling point, density and refractive index of a variety of compounds for which derivatives are difficult to prepare or are not recorded in the literature. The compounds are arranged alphabetically in this table and according to class in the preceding tables.

Name of Compound	B. P.	Sp. Gr.	n_D
1-Chloro-2-propanol.....	127°	1.1128 ²⁰ / ₂₀	1.4392
2-Chloro-1-propanol.....	132	1.103 ²⁰ / ₂₀	1.4362
β,β' -Dichloroethyl ether.....	179	1.2220 ²⁰ / ₂₀	1.4555
Diethylene glycol.....	245	1.1184 ²⁰ / ₂₀	1.4475
Diethylene glycol diethyl ether.....	188	0.9094 ²⁰ / ₂₀
Diethylene glycol mono- <i>n</i> -butyl ether.....	231	0.9554 ²⁰ / ₂₀	1.4290
Diethylene glycol mono- <i>n</i> -butyl ether acetate.....	246	0.9871 ²⁰ / ₂₀	1.4238
Diethylene glycol monoethyl ether.....	202	0.9898 ²⁰ / ₂₀	1.4244
Diethylene glycol monoethyl ether acetate.....	218	1.0114 ²⁰ / ₂₀	1.4180
Diethylene glycol monomethyl ether.....	193	1.0354 ²⁰ / ₂₀	1.4264
Di-(2-hydroxyethyl)-amine (Diethanolamine).....	268	1.0385 ²⁰ / ₂₀	1.4776
Diisobutyl ketone.....	168	0.810 ²⁰ / ₂₀	1.412
Dioxane.....	102	1.0353 ²⁰ / ₂₀	1.4221
2-Ethyl-1-butanol.....	149	0.8328 ²⁰ / ₂₀
α -Ethyl- <i>n</i> -butyraldehyde.....	116	0.8230 ²⁰ / ₂₀
α -Ethyl- <i>n</i> -butyric acid.....	197	0.9225 ²⁰ / ₂₀
α -Ethyl- <i>n</i> -caproaldehyde.....	163
α -Ethyl- <i>n</i> -caproic acid.....	224	0.9077 ²⁰ / ₂₀
Ethylene glycol diacetate.....	190	1.1063 ²⁰ / ₂₀	1.415
Ethylene glycol diethyl ether.....	121	0.8424 ²⁰ / ₂₀
Ethylene glycol mono- <i>n</i> -butyl ether.....	171	0.9019 ²⁰ / ₂₀	1.4191
Ethylene glycol monoethyl ether.....	135	0.9311 ²⁰ / ₂₀	1.4060
Ethylene glycol monoethyl ether acetate.....	156	0.9749 ²⁰ / ₂₀	1.4030
Ethylene glycol monomethyl ether.....	125	0.9664 ²⁰ / ₂₀	1.4028
Ethylene glycol monomethyl ether acetate.....	144	1.0067 ²⁰ / ₂₀	1.4016
Ethylene glycol monophenyl ether.....	245	1.1094 ²⁰ / ₂₀	1.534
2-Ethyl-1-hexanol.....	184	0.8344 ²⁰ / ₂₀	1.4300
2-Ethyl-1-hexyl acetate.....	199	0.8733 ²⁰ / ₂₀	1.4204
2-Hydroxyethylamine.....	170	1.0179 ²⁰ / ₂₀	1.4539
Isophorone.....	214	0.9255 ^{20.5} / ₄	1.4766
Methylisobutylcarbinol.....	132	0.8072 ²⁰ / ₂₀	1.4089
Methylisobutylcarbinol acetate.....	147	0.8805 ²⁰ / ₂₀
4-Methyl-2-pentanol.....	131	1.1593 ²⁰ / ₂₀	1.4068
Propylene chloride.....	98	1.1593 ²⁰ / ₂₀	1.4388
Propylene glycol.....	187	1.0381 ²⁰ / ₂₀	1.4293
Thiophene.....	84	1.0617 ²⁰ / ₄	1.5246
Trichloroethylene.....	90	1.4655 ²⁰ / ₂₀	1.4735
Triethylene glycol.....	288	1.1254 ²⁰ / ₂₀
Tri-(2-hydroxyethyl)-amine (Triethanola- mine).....	201(5 mm.)	1.1258 ²⁰ / ₂₀	1.4852

CHAPTER X

THE SEPARATION OF MIXTURES

The separation of mixtures of organic compounds is a problem with which the chemist is constantly confronted and for which he has developed a wide variety of solutions. Most of the procedures which are used are dealt with in elementary treatises on laboratory methods. Certain types, however, come naturally within the scope of the present book—namely, those that depend on differences in solubility and on the behavior of the components toward certain chemical reagents. In accord with this point of view, the methods of separation considered here will be limited to those that *take cognizance of the chemical character of the compounds to be separated*.

Devices of the type in question are numerous, but the underlying principle in all of them is the same. It involves taking advantage of a marked difference in the *polar character* of the compounds to be separated. In many cases this difference must be induced by some simple transformation—usually salt formation. Once the requisite difference in polarity is established separation can be effected by steam distillation or extraction methods.

BINARY MIXTURES

A. Separations Based on Salt Formation

The basic principle can be made clear by reference to simple examples. The separation of aniline from benzene is effected by extraction with dilute hydrochloric acid. The aniline goes into the aqueous layer in the form of its salt, aniline hydrochloride. Whereas aniline is very soluble in benzene and nearly insoluble in water, its salt—owing to its polar nature—is soluble in water and insoluble in benzene. Similarly, phenol is removed from benzene by shaking the mixture with a dilute sodium hydroxide solution. The phenol is transformed into its salt, sodium phenoxide, whose

highly polar character makes it insoluble in benzene and soluble in water. Benzaldehyde may be separated from benzene by a similar scheme. In this case the mixture is shaken with an aqueous solution of sodium bisulfite which converts the aldehyde into its bisulfite derivative. This is a typical salt and, therefore, insoluble in benzene but soluble in water. In each of these examples the original acid, base, or aldehyde is easily recovered by decomposition of the salt by familiar methods.

If the compounds to be separated are soluble to any considerable degree in water, extraction methods have a limited value. Steam distillation, however, can generally be used instead. For example, a mixture of acetic acid and cyclohexanone can be separated by adding enough alkali to transform the acid to sodium acetate and steam-distilling the mixture. The ketone will be removed in the distillate while the salt, being non-volatile, remains behind. Acidification with phosphoric acid regenerates the organic acid, which can now be distilled with steam.

Diethylamine can be separated from *n*-butyl alcohol in a similar manner. Phosphoric acid is added in sufficient amount to neutralize the base. Steam distillation will now remove the alcohol, and the amine can be recovered by adding sodium hydroxide to the residue and repeating the steam distillation.

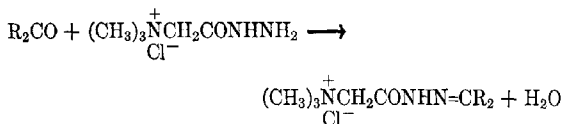
Another useful expedient for establishing a marked difference in the polar character of the components is illustrated by the separation of mixtures of primary amines from tertiary amines. Acetylation or benzoylation converts the primary amine to a *neutral* amide. Extraction with dilute hydrochloric acid will now remove the tertiary amine and leave the amide behind. The amide can be reconverted to the original amine by hydrolysis.

An almost exactly similar principle is involved in the Hinsberg method of separating primary and secondary amines. The sulfonamide from the primary amine forms a salt with alkalies and so can be removed by extraction with dilute sodium hydroxide solution.

A general method for separating acidic compounds is seen in the difference between Class A₁ and Class A₂ compounds. The former (strong acids) form salts when treated with sodium bicarbonate and can, accordingly, be extracted with this reagent. Thus, if a mixture of *o*-cresol and benzoic acid is shaken with a dilute solution of sodium bicarbonate the acid passes into the water layer as sodium benzoate, leaving the weakly acidic cresol behind.

A useful variant of the foregoing type of separation is to convert both the strong and the weak acids to salts and pass carbon dioxide through the solution. This produces sodium bicarbonate and causes the weakly acidic substance to separate. Obviously, any compound less acidic than carbonic acid can be removed in this way.

A very ingenious device for separating aldehydes or ketones from other neutral and water-insoluble compounds is illustrated by the use of Girard's reagent, betaine hydrazide hydrochloride ($((\text{CH}_3)_3\text{N}^+\text{CH}_2\text{CONHNH}_2)\text{Cl}^-$). It reacts with the carbonyl compound after the manner of simple hydrazides. The product, however, being a quaternary ammonium salt, is extremely polar and therefore soluble in water.



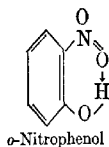
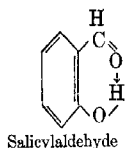
Extraction with ether removes the water-insoluble compounds, leaving the salt in the aqueous layer. Hydrolysis reconverts it to the original carbonyl compound.

B. Multiplicity of Functional Groups

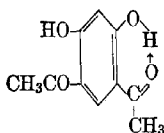
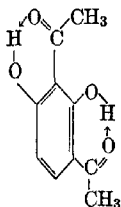
A difference in polarity sufficient to permit separation by steam distillation is generally provided by a second functional group in the molecule. Thus monatomic alcohols can be separated from diatomic and polyatomic alcohols by this scheme. Similarly simple acids, amines, and many other volatile compounds can be separated from the corresponding di- and polyfunctional compounds. Moreover, the additional group or groups need not be the same as the original. Amino acids, hydroxy acids, nitro acids, keto acids, keto alcohols, and cyano ketones are rarely volatile with steam. In fact, it is a general rule that the presence in a molecule of two or more functional (polar) groups will render a compound non-volatile. Volatile S_1 compounds can always be separated in this manner from any S_2 compounds. Table XLVI shows which types

of compounds are volatile with steam and which are not. Acetic acid and oxalic acid, ethyl alcohol and ethylene glycol, benzoic acid and phthalic acid are mixtures which illustrate the point. In each pair the first named can be removed by steam distillation while the other remains behind.

A very interesting group of exceptions to the multiple-function rule is found in the aromatic series, however. *o*-Nitrophenol, salicylaldehyde, and many other *ortho* disubstituted benzene derivatives are volatile with steam. The explanation for this apparently anomalous loss of polar character is found in the observation that *all these exceptional compounds are capable of existing in chelated forms*. As is well known, the chelated compounds tend to be non-polar. The chelated structures of *o*-nitrophenol and salicylaldehyde are shown below.



A very remarkable example of this diminution of polar properties by chelation is found in the isomeric 2,4- and 4,6-diacetyl-resorcinols. The former melts at 91° and is volatile with steam; the latter melts at 182° and is not volatilized by steam. It will be seen that if we use the Kekulé structure only one chelate ring is possible in the 4,6-isomer but two can be present in the 2,4-derivative.



The assumption is made that chelation is possible only if a double bond is between the hydroxyl and acetyl groups involved.

TABLE XLVI

Solubility Class	Solubility	Types of Compounds	Volatility Alone	Volatility with Steam
S ₁	Soluble in water and ether.	Low-molecular-weight alcohols, aldehydes, ketones, acids, esters, amines, nitriles, acid chlorides.	Readily distil. Many compounds boil below 100°.	Volatile with steam.
S ₂	Soluble in water but insoluble in ether.	Polyhydroxy alcohols, diamines, carbohydrates, amine salts, metal salts, polybasic acids; hydroxy-aldehydes, -ketones, and -acids; amino acids.	Low volatility. With certain exceptions these compounds cannot be distilled at atmospheric pressure.	Not volatile with steam.
A ₁	Insoluble in water. Soluble in NaOH and NaHCO ₃ .	High-molecular-weight acids; negatively substituted phenols.	Low volatility.	Usually not volatile but there are some exceptions.
A ₂	Insoluble in water and NaHCO ₃ but soluble in NaOH.	Phenols, sulfonamides of primary amines, primary and secondary nitro compounds; imides, thiophenols.	High boiling points. Many cannot be distilled.	Usually not volatile.
B	Insoluble in water but soluble in dilute HCl.	Amines containing not more than one aryl group attached to nitrogen; hydrazines.	High boiling points.	Many are volatile with steam.
M	Insoluble in water, dilute NaOH, and HCl, but contain elements other than carbon, hydrogen, oxygen and the halogens.	Nitro compounds (<i>tert</i>), amides, negatively substituted amines; sulfonamides of secondary amines; azo and azoxy compounds; alkyl or aryl cyanides, nitrites, nitrates, sulfates, phosphates.	High boiling points. Many cannot be distilled.	Some are volatile with steam.
N ₁	Insoluble in water, dilute NaOH and HCl, but soluble in both H ₂ SO ₄ and H ₃ PO ₄ .	Alcohols, aldehydes, methyl ketones and esters having fewer than nine carbon atoms.	Boil higher than compounds in S ₁ but generally lower than compounds in N ₂ .	Volatile with steam.
N ₂	Insoluble in water, dilute NaOH, dilute HCl and H ₃ PO ₄ , but soluble in H ₂ SO ₄ .	Alcohols, aldehydes, ketones and esters having more than nine carbon atoms; unsaturated compounds.	High-boiling compounds.	Usually volatile with steam.
I	Insoluble in water, dilute NaOH, dilute HCl, H ₃ PO ₄ and H ₂ SO ₄ .	Aromatic and aliphatic hydrocarbons and their halogen derivatives.	Volatile.	Volatile with steam.

The introduction of several polar functional groups into a molecule causes a decrease in the solubility in non-polar solvents such as ether, ligroin, carbon tetrachloride, and benzene (p. 68). Hence it is frequently possible to separate a Class S_1 compound from a Class S_2 compound by treatment with absolute ether. Treatment with a non-polar solvent may be of use also in separating compounds in other solubility classes. For example, benzoic acid is much more soluble in ether than is terephthalic acid. Phenyl- and α -naphthylurethans are soluble in warm ligroin or carbon tetrachloride, whereas *sym*-diphenylurea and *sym*-di- α -naphthylurea are insoluble. Treatment with ligroin, therefore, offers a means of separation, and advantage is taken of this fact in the purification of urethans (p. 164).

It was pointed out in Chapter VI that hydrogen bonding between solute molecules and between solute and solvent is an important factor controlling solubility. Compounds possessing functional groups which act only as donors in hydrogen-bond formation are very soluble in chloroform but not especially so in hexane or carbon tetrachloride. Use can be made of this fact in separating mixtures.

C. Special Devices

Aromatic hydrocarbons are frequently separated from paraffinic or alicyclic hydrocarbons by treatment with fuming sulfuric acid. This converts the aromatic component to a highly polar sulfonic acid which can be separated and reconverted to the hydrocarbon by treatment with superheated steam.

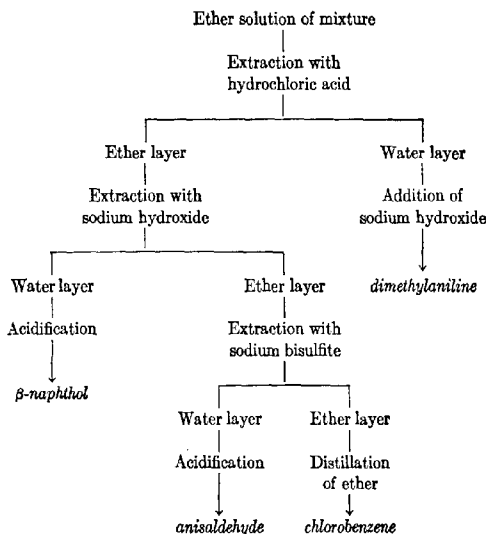
SEPARATION OF MIXTURES CONTAINING THREE OR MORE COMPONENTS

If a mixture contains more than two compounds, combinations of the foregoing methods frequently lead to satisfactory separations. The necessary condition for successful separation is that *the components be of such nature that a wide polarity difference exists or can be induced between any two of them.*

In practice mixtures fall into two categories, depending on whether they are soluble in water. These two types will be considered separately.

Water-insoluble Mixtures

A mixture of chlorobenzene, dimethylaniline, β -naphthol, and anisaldehyde will illustrate the water-insoluble type. It could be separated according to the following scheme. To minimize mechanical losses and facilitate handling the mixture should first be dissolved in ether.

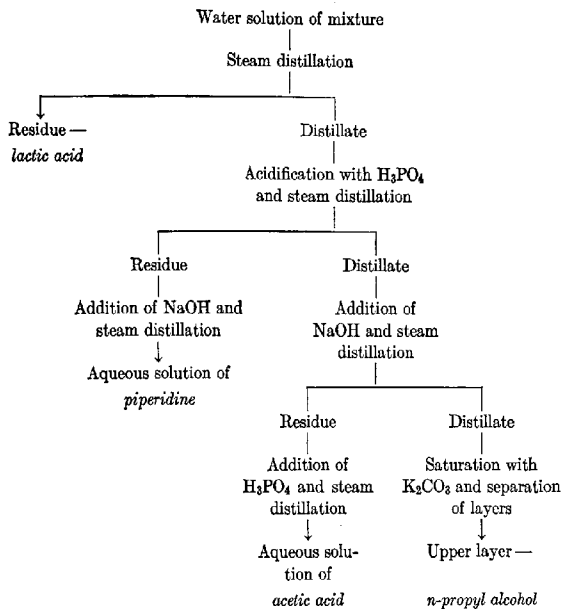


A general procedure for this type of mixture is outlined on page 293. It is suitable only for mixtures no component of which is soluble in water.

Water-soluble Mixtures

If all the components of the mixture are water-soluble, extraction must be replaced by steam distillation as was indicated in the discussion of water-soluble binary mixtures. An illustration of this type of separation is afforded by a mixture of piperidine, lactic

acid, acetic acid, and *n*-propyl alcohol. This separation may be effected by the following scheme.



The general method for separating water-soluble mixtures is outlined on page 290.

LABORATORY PROCEDURES FOR THE SEPARATION OF MIXTURES

The identification of the components of a mixture involves first a separation into individual compounds and second the characterization of each of the latter according to the procedures in the foregoing chapters. It is very rarely possible to identify the constituents of a mixture without previous separation. The separation of the compounds in a mixture should be as nearly quantitative as possible in order to give some idea of the actual percentage

of each component. It is far more important, however, to carry out the separation in such a manner that each of the compounds is obtained in the pure state since this renders the individual identification much easier.

It is desirable that the method of separation chosen be such that the compounds are obtained as they existed in the original mixture. Derivatives of the original compounds are not very useful unless they may be reconverted readily into the original compounds. This criterion of separation is necessary because the identification of a compound rests ultimately on agreement between physical constants of the original and of a derivative with similar data obtained from the literature.

The origin and history of a mixture will usually furnish sufficient information to indicate the group to which the mixture belongs and hence the general mode of separation to be used.

Preliminary Examination of Mixtures

1. The physical state is noted. If a solid is suspended in a liquid, the solid is removed by filtration and is examined separately. If two immiscible liquids are present they likewise are separated and examined individually.

2. The solubility or insolubility of the mixture in water is determined.

3. With liquid mixtures, 2 ml. of the solution is evaporated to dryness on a watch crystal or porcelain crucible cover and the presence or absence of a residue noted. The ignition test is applied to the residue. For a solid mixture the ignition test is applied directly.

4. In liquid mixtures the presence or absence of water is detected by: (a) determining the miscibility of the solution with ether; (b) anhydrous copper sulfate; (c) distillation test for water. The distillation test is the most reliable and is carried out in the following manner. Five milliliters of the liquid mixture and 5 ml. of anhydrous toluene are placed in a small distilling flask. The mixture is heated gently until distillation occurs, and 2 ml. of distillate is collected. About 5 to 10 ml. of anhydrous toluene is added to the distillate. The presence of two layers or distinct

drops suspended in the toluene indicates water. If the solution is only cloudy, traces of water are indicated.

5. If water has been found to be absent, the presence or absence of a volatile solvent in a liquid mixture is determined by placing 10 ml. of the mixture in a 25-ml. distilling flask. The flask is placed in a beaker of cold water which is heated to boiling. Any liquid that distills under these conditions is classified as a volatile solvent. The distillate, which may be a mixture of readily volatile compounds, and the residue in the flask are examined separately.

It frequently happens that distillation of a mixture originally water-soluble yields a volatile solvent and a water-insoluble residue. The separation of such a mixture is, therefore, carried out by removing all the volatile solvent. The residue is then treated as a water-insoluble mixture.

If the residue after distillation is a water-soluble liquid it is best not to remove the solvent at this stage since the separation is usually not quantitative.

If, however, the residue after distillation is a water-soluble solid and the removal of the solvent seems quantitative, then it is desirable to remove all the volatile solvent and to examine distillate and residue separately.

It is to be noted that if water is present no such separation should be attempted.

6. The reaction of an aqueous solution or suspension of the mixture to litmus and phenolphthalein is determined. If the mixture is distinctly acid, 5 ml. should be titrated with 0.1 *N* sodium hydroxide solution in order to determine whether considerable amounts of free acid are present or whether the acidity is due to traces of acids formed by hydrolysis of esters. The titration must be performed in an ice-cold solution and the first pink color of phenolphthalein taken as the end point.

7. Two milliliters of the mixture is acidified with hydrochloric acid, and the solution is cooled. The evolution of a gas or the formation of a precipitate is noted. Dilute sodium hydroxide solution is now added, and the result is noted.

8. Two milliliters of the mixture is made distinctly alkaline with sodium hydroxide solution. The separation of an oil or solid, the liberation of ammonia, and any color changes are noted. The

solution should be heated just to boiling and then cooled. The odor is now compared with that of the original mixture. The presence of esters is often indicated by a change in odor. Dilute hydrochloric acid is now added, and the result is noted.

9. In the case of water-insoluble mixtures an elementary analysis should be made. If water or a large amount of a volatile solvent is present in a water-soluble mixture the elementary analysis of the mixture is omitted. If the water-soluble mixture is composed of solids an elementary analysis is made.

10. If water is absent the effect of the following classification reagents is cautiously determined: (a) metallic sodium; (b) acetyl chloride.

11. The action of the following classification reagents should be determined on an aqueous solution or suspension of the original mixture: (a) bromine water; (b) potassium permanganate solution; (c) ferric chloride solution; (d) alcoholic silver nitrate solution; (e) fuchsin-aldehyde reagent; (f) phenylhydrazine.

At this stage of the examination the results of the above tests are summarized and as much information as possible is deduced from the behavior of the mixture. The preliminary study will show the group in which the mixture should be classified and will, therefore, indicate which of the following procedures should be used in its separation.

Mixtures of Water-soluble Compounds

The schematic diagram on page 291 represents one method for the separation of this type of mixture. It may and should be modified for certain mixtures when the preliminary examination indicates that such modification is expedient.

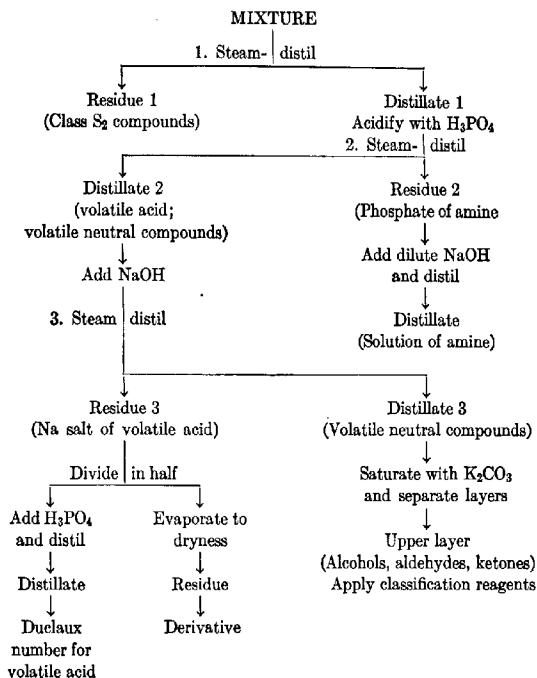
PROCEDURE

1. About 50 ml. of the mixture is placed in a 500-ml. round-bottomed flask arranged for steam distillation. A steam trap and safety tube should be used. By means of steam distillation from 50 to 60 ml. of distillate 1 is collected. Residue 1 in the flask is placed in an evaporating dish, and the water is evaporated by means of a steam cone. Occasionally the last traces of water may

best be removed under diminished pressure. The residue, liquid or solid, is examined for compounds in Class S_2 .

2. Distillate 1 is acidified with phosphoric acid and steam-distilled to yield 40 to 50 ml. of distillate 2. Residue 2, consisting

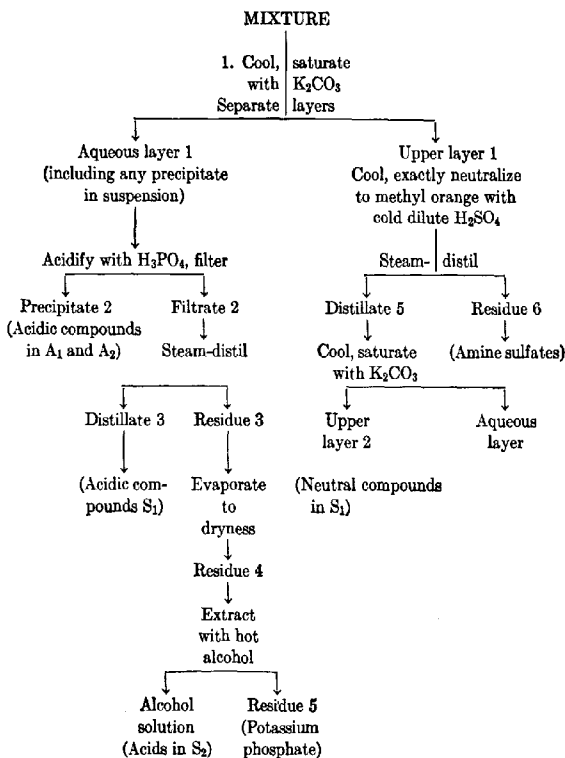
MIXTURES OF WATER-SOLUBLE COMPOUNDS



of the phosphate of the amine, is made alkaline, and the amine is distilled. If the amine is very volatile it should be collected in hydrochloric acid and isolated as the hydrochloride. Less volatile amines may be separated from the aqueous solution by means of potassium carbonate.

3. Distillate 2 is made just slightly alkaline with dilute sodium hydroxide solution and is again steam-distilled, 30 to 40 ml. of distillate 3 being collected. Residue 3 (in the flask) is composed of

WATER-SOLUBLE MIXTURES CONTAINING ESTERS



the sodium salt of the acidic compound of Class S_1 . Half of it is acidified with phosphoric acid and steam-distilled. Duclaux numbers are determined on the distillate. The other half of the solution of the sodium salt is used for the preparation of a derivative.

4. Distillate 3 contains volatile neutral compounds—alcohols, aldehydes, and ketones. These may be separated from the water by saturation with potassium carbonate. Classification reagents are applied to determine whether one or all of these are present. If only one is present, the liquid is distilled, the boiling point is noted, and a derivative is prepared.

Discussion. In the first steam distillation it should be remembered that amine salts of weak acids (e.g., aniline acetate) may undergo hydrolysis to such an extent that both acid and base will be found in the distillate. Salts of strong acids (e.g., aniline hydrochloride) are unaffected by steam distillation; they remain behind in the distilling flask.

Note that the procedure outlined above would cause hydrolysis of any esters that might be present. If the presence of an ester is indicated by odor or by change of odor in preliminary test 8, the procedure may be modified as indicated on page 292.

If the mixture contains no acidic constituents the separation may start at the same point as the treatment of upper layer 1. In such a case residue 6 may contain acidic compounds (which were originally present as salts) in groups S₂, A₁, or A₂ in addition to the amine sulfates. It may be separated by the first method given.

This modified procedure may also be used to advantage with mixtures containing acids and alcohols; it provides no opportunity for esterification to take place. (See diagram on page 292.)

Mixtures of Water-insoluble Compounds

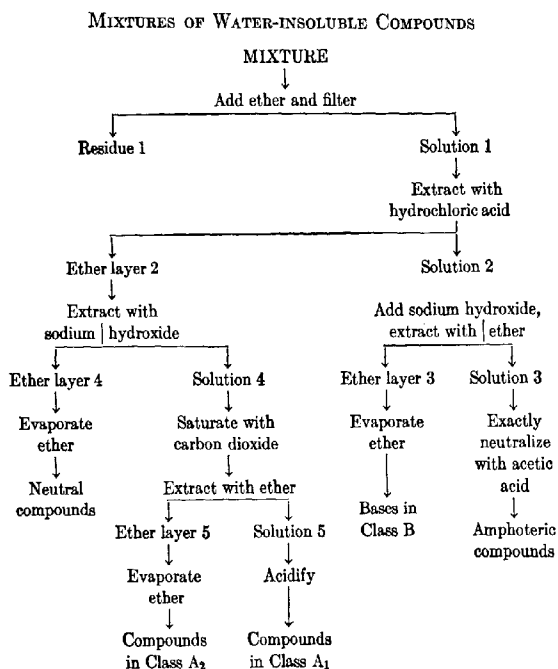
After the removal of any volatile solvent the following procedure may be used for the separation of a water-insoluble mixture. (See page 294.)

PROCEDURE

From 25 to 50 g. of the mixture is mixed with 75 ml. of ether, and any insoluble compounds (residue 1) are separated on a filter and washed with ether. The ether washings are added to the original ether solution, and the ether solution (1) is then extracted with three 30-ml. portions of 5% hydrochloric acid solution. If a solid amine hydrochloride separates during this extraction, the

hydrochloric acid should be diluted with water until a solution results.

The hydrochloric acid extracts are combined (solution 2) and rendered alkaline with sodium hydroxide solution, and the resulting mixture is extracted with several 25-ml. portions of ether. The



ether layer (3) is dried with sodium sulfate, and the ether is distilled. The residue is composed of bases in Class B.

The solution (3) after ether extraction is carefully neutralized with acetic acid. If a solid separates it may be removed by filtration, but it is better to extract the solution four or five times with 25-ml. portions of ether in order to recover any amphoteric compounds (Classes A₁(B) and A₂(B)).

The ether layer (2) from the hydrochloric acid extraction is now extracted with three 30-ml. portions of 5% sodium hydroxide solution. If a soapy emulsion is formed, more water and a little alcohol may be added in order to cause the separation of two layers.

The ether layer (4) is dried with sodium sulfate, and the ether is distilled. The residue contains the neutral compounds (Classes N_1 and N_2), the indifferent compounds (Class I), and miscellaneous compounds (Class M). Classification reagents should be applied as well as tests designed to determine whether or not the residue is a mixture. This mixture may often be further separated by a steam distillation. If an aldehyde is present it should be extracted by means of sodium bisulfite solution, with the addition of ether to facilitate separation. If the residue is a solid it may often be fractionally crystallized from alcohol. If the residue is a liquid and no chemical separation appears possible it may be fractionally distilled.

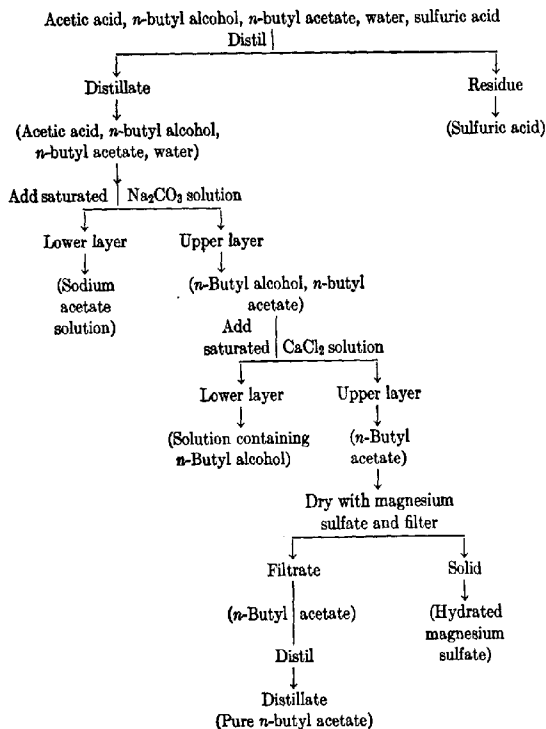
The sodium hydroxide solution (4) is cooled and saturated with carbon dioxide. Any compounds in Class A_2 are extracted with several portions of ether (ether layer 5). To remove any dissolved ether, solution 5 is warmed on a steam cone for a few minutes and stirred. It is then acidified and cooled; the compounds in Class A_1 are then removed by filtration or by extraction with ether.

Mixtures Encountered in Synthetic Work

Every student has already separated many mixtures during his first year's laboratory work in organic chemistry. The principles used in devising procedures for the isolation and purification of an organic compound from a reaction mixture are identical with those which have been pointed out in the preceding chapters. In fact, the very great improvement in the yields of organic compounds obtainable from a given reaction has been due to the application of knowledge concerning solubility and behavior toward classification reagents to the outlining of the most efficient method of separation.

The following procedures used in beginning courses in organic chemistry illustrate the separation of mixtures encountered in synthetic work.

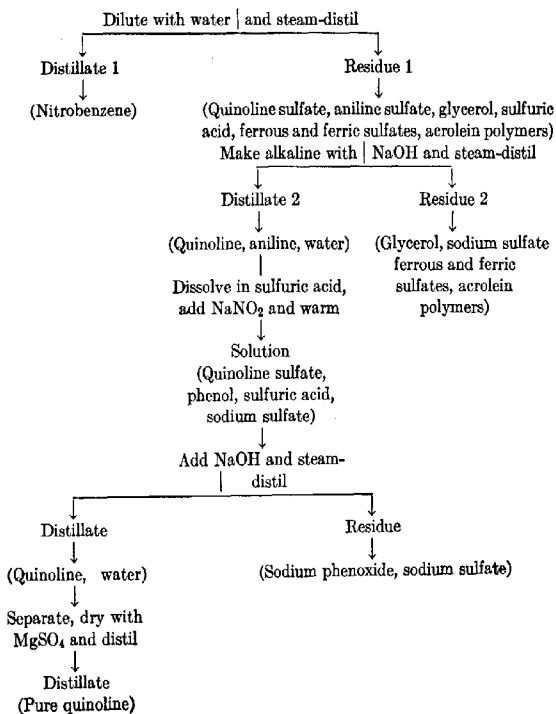
MIXTURE



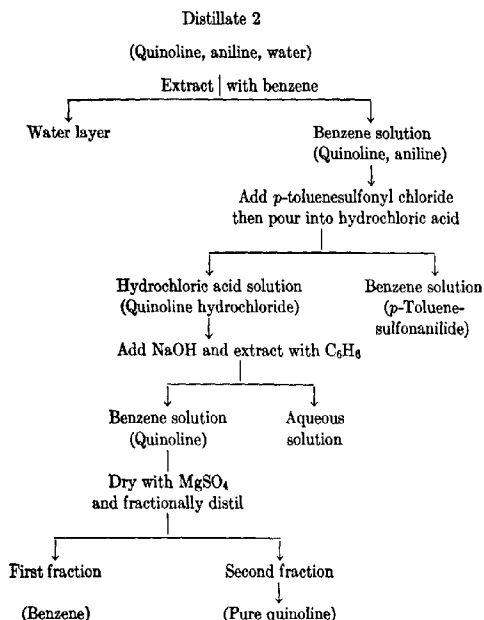
The Preparation of Quinoline. Skraup's reaction produced a mixture composed chiefly of the compounds shown below which was separated as follows:

MIXTURE

Quinoline sulfate, aniline sulfate, nitrobenzene, glycerol, sulfuric acid, ferrous and ferric sulfates, acrolein polymers



ALTERNATIVE PROCEDURE FOR PURIFICATION OF QUINOLINE



EXERCISES

I. Diagram a satisfactory procedure for the separation of the following mixtures and the identification of each component.

1. Water, isopropyl alcohol, aniline sulfate, lactose, isobutyric acid.
2. Chloroform, aniline, benzoic acid, *N,N*-diethylaniline, naphthalene.
3. Benzene, diphenylamine, quinoline, nitrobenzene, *m*-dinitrobenzene.
4. Methyl alcohol, *o*-cresol, salicylic acid, methylaniline, *p*-toluidine, styrene, anthracene.
5. Carbon tetrachloride, benzaldehyde, salicylaldehyde, triphenylcarbinol, benzyl alcohol.
6. Ethyl ether, ethyl alcohol, acetone, diethyl ketone, diethylamine, acetic acid.
7. Diethylamine, 2,4-dibromoaniline, quinaldine, phthalimide, phenol, *p*-dichlorobenzene, benzamide.

8. Cyclohexane, *p*-toluidine, quinoline, 2-chloro-4-aminobenzoic acid, *m*-cresol, benzene, 3-nitro-5-bromoanisole.

9. A solid mixture of sodium benzoate, sodium oxalate, phenylhydrazine hydrochloride, benzoic acid, camphor.

10. An instructor mixed the following compounds in the order named and gave out this mixture as an unknown. What might the student expect to find? Diagram a possible separation of the actual components after the mixture had stood for a week (assume complete reactions). *tert*-Butyl alcohol (7.4 g.); benzyl alcohol (10.8 g.); benzaldehyde (10.6 g.); acetyl chloride (15.6 g.); acetophenone (12.0 g.); dimethylaniline (84.7 g.).

II. The following problems illustrate the separation of mixtures actually encountered during the course of the preparation of simple compounds. The essential starting materials and reagents are indicated. First make a list of the compounds produced as the result of the main and side reactions, and then diagram a procedure suitable for the separation of the compounds, starting with the crude reaction mixture. Next, compare your method with that described in the literature.

1. Ethyl ether was made by passing 95% alcohol through ethyl hydrogen sulfate at 145°.

2. *n*-Butyl bromide was made by refluxing *n*-butyl alcohol with aqueous hydrobromic-sulfuric acid solution.

3. Bromobenzene and *p*-dibromobenzene were made by the action of bromine on benzene in the presence of iron.

4. *p*-Bromonitrobenzene was made by the action of concentrated nitric and sulfuric acids on bromobenzene.

5. Ethylbenzene was made by the reaction between ethyl bromide and benzene in the presence of anhydrous aluminum chloride.

6. Aniline was made by the action of tin and hydrochloric acid on nitrobenzene.

7. *o*-Chlorotoluene was made by the Sandmeyer reaction from *o*-toluidine.

8. Benzyl alcohol and benzoic acid were made by the Cannizzaro reaction from benzaldehyde and aqueous potassium hydroxide.

9. Benzilic acid was made by the action of an aqueous solution of sodium hydroxide and sodium bromate on benzoin.

10. Ethyl *n*-butylacetoacetate was made by the alkylation of ethyl acetoacetate with *n*-butyl bromide in the presence of sodium ethoxide in absolute ethanol.

11. *n*-Amyl methyl ketone was made by the hydrolysis of ethyl *n*-butylacetoacetate.

CHAPTER XI

THE INTERPRETATION OF EXPERIMENTAL DATA

The laboratory examination of an organic compound results in the accumulation of data concerning the physical properties, notably solubility, and behavior toward certain suitable class reagents and in various special tests. All these observed facts must be correlated and interpreted in order to arrive at possible structural formulas for the compound in question. It is necessary not only to establish the general class to which a compound belongs but also to make deductions concerning the entire structure, the probable relative position of the functional groups, and the nature of the nucleus to which they are attached. Careful examination of the data will frequently serve to exclude a large number of compounds from consideration and leave a relatively few structures as possibilities. The final proof, of course, is dependent on the preparation of unique derivatives.

It is the purpose of the present discussion to point out, by means of several specific examples, the mode of attack and reasoning involved in deducing information concerning the structure of a molecule from experimental data. The ability to relate laboratory observations to molecular structure is useful in identifying known compounds and is especially important in identifying new compounds.

Two very helpful special tests described in Chapter VII are the determinations of the neutralization equivalents of acids and bases and saponification equivalents of esters. These numerical data, in conjunction with the solubility class and behavior towards reagents, frequently give valuable clues concerning the molecular structure of the compound. Their use may best be explained by reference to examples.

Example 1. An organic acid has a neutralization equivalent of 45 ± 1 .

As pointed out previously (p. 129) the neutralization equivalent of an acid is dependent on the number of carboxyl groups in the

molecule. If one carboxyl group is present, the neutralization equivalent is equal to the molecular weight. If the present compound is monobasic its molecular weight¹ must be 44, 45, or 46. A carboxyl group weighs 45; hence if the molecular weight were 45 there could be nothing attached to the carboxyl radical. A molecular weight of 44 is obviously impossible, but a molecular weight of 46 leaves a residue of 1 after subtracting the weight of the carboxyl radical. Only one element has the atomic weight of 1; hence, formic acid (HCOOH) is one possibility.

However, the compound might be dibasic, in which event the molecular weight would be 90 ± 2 . Two carboxyl groups equals $2 \times 45 = 90$. Hence, a possible residue of 0, 1, or 2 units remains. There are no bivalent atoms of this atomic weight; hence the only possible dibasic acid is oxalic acid, in which the two carboxyl groups are united: COOH . Thus, by assuming first a monobasic acid



and then a dibasic acid, two possible structures have been deduced from the neutralization equivalent alone. In order to decide between the two, the physical state or the solubility class of the compound would serve. If this compound with a neutralization equivalent of 45 ± 1 is a liquid in Class S_1 , it must be formic acid; if a solid in Class S_2 , it must be anhydrous oxalic acid.

Consideration of the molecular weights indicates in a similar fashion that the compound could not be tribasic (mol. wt., 135 ± 3) or tetrabasic (mol. wt., 180 ± 4).

Example 2. A compound (A) in solubility Class A_1 possessed a neutralization equivalent of 136 ± 1 . It gave negative tests for halogen, nitrogen, and sulfur. It did not decolorize cold potassium permanganate solution; but, when an alkaline solution of the compound was refluxed with this reagent for an hour and acidified, a new compound (B) was precipitated. This compound had a neutralization equivalent of 83 ± 1 .

¹ For purposes of illustration and calculation in this chapter whole numbers have been used for the atomic weights of the elements carbon, hydrogen, oxygen, nitrogen, and bromine. The actual atomic weights (which must be used in all precise quantitative analyses) differ from these rounded-off values by an amount less than the experimental error involved in the determination of neutralization and saponification equivalents.

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First consider the compound B. Assume it to be monobasic.

$$\begin{array}{r} \text{Molecular weight} = 83 \pm 1 \\ \text{Less one } -\text{COOH} = 45 \\ \hline \text{Residue} = 38 \pm 1 \end{array}$$

This residue to which the carboxyl group is attached must be made up of some combination of carbon, hydrogen, and perhaps oxygen which is stable to hot potassium permanganate solution. Examination shows that this is not possible.

$$\begin{array}{r} \text{Residue} = 38 \pm 1 \\ \text{Three carbon atoms} = 3 \times 12 = 36 \\ \hline \text{Remainder} = 2 \pm 1 \end{array}$$

The residue might be C_3H , C_3H_2 , or C_3H_3 , none of which corresponds to a compound which would be stable to permanganate. The paraffin would require C_3H_8 as the parent compound, and the alkyl radical would have to be C_3H_7 ; similarly the cycloparaffin would have to be C_3H_6 and the cyclopropyl radical C_3H_5 .

The presence of oxygen in this residue is also excluded. If it is assumed to be present, the following figures are obtained.

$$\begin{array}{rcl} \text{Residue} = 38 \pm 1 & \text{or} & \text{Residue} = 38 \pm 1 \\ \text{One oxygen atom} = 16 & & \text{Two oxygen atoms} = 32 \\ \hline & & \hline & & \text{Remainder} = 6 \pm 1 \\ 22 \pm 1 & & \\ \hline \text{One carbon atom} = 12 & & \\ \hline \text{Remainder} = 10 \pm 1 \end{array}$$

Neither of these remainders corresponds to any atom or groups of atoms. Thus, it is now safe to conclude that the compound B *cannot be monobasic*.

Assume compound B to be dibasic.

$$\begin{array}{r} \text{Molecular weight} = 2 \times 83 \pm 1 = 166 \pm 2 \\ \text{Two carboxyl groups} = 90 \\ \hline \text{Residue} = 76 \pm 2 \end{array}$$

If this residue is paraffinic it must be made up of $-(\text{CH}_2)-$ units

$$\begin{array}{r} \text{Five } -\text{CH}_2- = 5 \times 14 = 70 \\ \text{Six } -\text{CH}_2- = 6 \times 14 = 84 \end{array}$$

Neither of these corresponds to the weight of the residual radical, 76 ± 2 .

Another grouping which is stable to hot permanganate is the benzene nucleus. This is an arrangement of six CH groups or $6 \times 13 = 78 =$ molecular weight of benzene itself. If two carboxyl groups are present, two of the hydrogen atoms are displaced and the residue becomes $78 - 2 = 76$. This value checks that calculated above for the residue, and hence a possible structure for B is $C_6H_4(COOH)_2$; i.e., it may be one of the phthalic acids.

The question now arises whether compound B could be tribasic. If so we have the following values:

$$\begin{array}{rcl} \text{Molecular weight} & = & 3 \times 83 \pm 1 = 249 \pm 3 \\ \text{Three carboxyl groups} & = & 3 \times 45 \quad = 135 \\ \hline \text{Residue} & = & 114 \pm 3 \end{array}$$

Inspection shows that this residue cannot be aromatic since it does not correspond to one or more benzene rings. A benzene ring plus a side chain is excluded since the side chain would be oxidized by the permanganate. The value 114 ± 3 does correspond, however, to eight $-CH_2-$ groups within the experimental error ($8 \times 14 = 112$). Hence $C_8H_{15}(COOH)_3$ with a molecular weight of 246 falls within the limit of 249 ± 3 . Although this tricarboxylic acid represents a possible structure for a compound with a molecular weight of 249 ± 3 it will be seen that it would be impossible to produce it from the compound A which has a neutralization equivalent of 136 ± 1 .

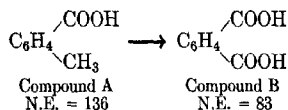
Assume that A is monobasic.

$$\begin{array}{rcl} \text{Molecular weight A} & = & 136 \pm 1 \\ \text{One } -COOH & = & 45 \\ \hline \text{Residue} & = & 91 \pm 1 \end{array}$$

Since B has a C_6H_4 grouping stable to permanganate this same group must be present in A also.

$$\begin{array}{rcl} \text{Residue} & = & 91 \pm 1 \\ C_6H_4 & = & 76 \\ \hline \text{Remainder} & = & 15 \pm 1 \end{array}$$

This remainder of 15 ± 1 corresponds to a methyl group which must be attached to the ring.

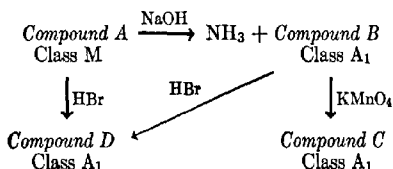


The original must be *o*-, *m*-, or *p*-toluic acid, each of which would give the reactions cited. Additional data, such as a melting point or a derivative, are necessary to distinguish between them.

This example also illustrates the fact that oxidation almost invariably converts a compound with a given neutralization equivalent to a product which has a lower neutralization equivalent. This generalization follows naturally from the increase in the number of carboxyl groups or cleavage of the molecule into smaller fragments.

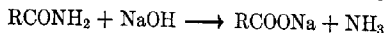
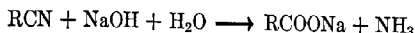
Example 3. A colorless crystalline compound (A) gave a positive test for nitrogen but not for halogens or sulfur. It was insoluble in water, dilute acids, and alkalis. It reacted with acetyl chloride but not with phenylhydrazine. Compound A dissolved in hot sodium hydroxide solution with the liberation of ammonia and the formation of a clear solution. Acidification of this solution produced compound B, which contained no nitrogen and gave a neutralization equivalent of 182 ± 1 . Oxidation of B by hot permanganate solution produced C, which had a neutralization equivalent of 98 ± 1 . When either A or B was refluxed with hydrobromic acid for some time a compound D separated. This compound contained bromine but no nitrogen. It gave a precipitate with bromine water and a violet color with ferric chloride, and it readily reduced dilute potassium permanganate. It was soluble in sodium bicarbonate solution.

These reactions may be summarized in the following chart.

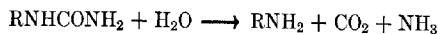


The elimination of nitrogen from compound A by alkaline hydrolysis suggests the presence of a nitrile or amide grouping

since these functional groups liberate ammonia when they undergo hydrolysis.



The imide grouping, $-\text{CONHCO}-$, which also liberates ammonia is excluded by the fact that compound A is in solubility Class M and not Class A₂. Since compound B contained no nitrogen, negatively substituted amines, such as 2,4-dinitroaniline, are excluded. The absence of nitrogen in B and the fact that it was acidic and not basic likewise eliminate a substituted urea which also liberates ammonia when hydrolyzed.



The positive acetyl chloride test suggests an alcohol; an amino or phenolic group is excluded by the fact that compound A is in Class M and not in Class B or Class A₂. Further evidence for the presence of a hydroxyl group is furnished by the fact that compound D, produced from A by the action of hydrobromic acid, contained bromine.



The properties of compound D strongly suggest the presence of a phenolic hydroxyl group. Ease of bromination, sensitivity to permanganate, and color with ferric chloride are properties characteristic of substituted phenols. This phenolic hydroxyl group was produced by the action of hydrobromic acid on some functional group present in A and B since neither of these originally contained the phenol grouping. One type of compound which produces a phenol when treated with hydrobromic acid is an aryl alkyl ether.



If the alkyl group is small, it would be lost as alkyl bromide during the refluxing with hydrobromic acid. Thus compounds A, B, and C probably contain such a mixed ether group and also an aromatic nucleus since the substituted phenol D contains one. The solubility of D in sodium bicarbonate solution is probably due to the presence of a carboxyl group since both the nitrile and amide groups are hydrolyzed to carboxyl groups by acids as well as alkalis. Hence compound D is an hydroxybenzoic acid with the

bromine attached to a side chain. This side chain must also be present in compound A with an alcoholic group in place of the bromine atom.

The neutralization equivalents of compounds B and C may now be considered. It will be noted that the neutralization equivalent of compound C produced by permanganate oxidation is lower than that of compound B which acquired its acidic properties by an hydrolysis reaction only. This oxidation obviously affects the side chain, and compound C must have more carboxyl groups than B.

Assume compound C to be dibasic.

$$\begin{array}{rcl}
 \text{Molecular weight} & = & 2 \times 98 \pm 1 = 196 \pm 2 \\
 \text{Two carboxyl groups} & = & 2 \times 45 = 90 \\
 & & \hline
 & & 106 \pm 2 \\
 \text{One oxygen atom in ether linkage} & = & 16 \\
 & & \hline
 & & 90 \pm 2 \\
 \text{Benzene minus 3 hydrogen atoms (C}_6\text{H}_3) & = & 75 \\
 & & \hline
 \text{Residue} & \approx & 15 \pm 2
 \end{array}$$

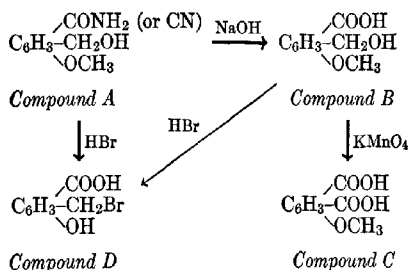
This residue of 15 corresponds to a CH_3- group, and hence the ether grouping must have been $\text{CH}_3\text{O}-$.

It is now necessary to find the length of the side chain to which the alcohol group in A and B is attached.

If C is dibasic, B is monobasic.

$$\begin{array}{rcl}
 \text{N. E.} & = & \text{Mol. Wt.} = 182 \pm 1 \\
 \text{Carboxyl group} & = & 45 \\
 & & \hline
 & & 137 \pm 1 \\
 \text{Methoxyl group} & = & 31 \\
 & & \hline
 & & 106 \pm 1 \\
 \text{Hydroxyl group} & = & 17 \\
 & & \hline
 & & 89 \pm 1 \\
 \text{Benzene nucleus (C}_6\text{H}_3) & = & 75 \\
 & & \hline
 \text{Residue} & = & 14 \pm 1
 \end{array}$$

This residue represents the weight of the aliphatic side chain and obviously corresponds to $-\text{CH}_2-$. Hence, possible structures for A, B, C, and D are:



This example illustrates the fact that a given reagent may affect more than one functional group. Thus, boiling hydrobromic acid affected three functional groups in compound A and two in compound B.

In the identification of new compounds, it is customary to run quantitative analyses for the elements and to determine the molecular weight. From these data the molecular formula may be calculated. By considering the molecular formulas of several compounds and the reactions which produced them one is frequently able to deduce possible formulas. The following problem involves the deduction of a large amount of information from only a few clues.

Example 4. A neutral compound (A) ($\text{C}_{15}\text{H}_{14}\text{O}$) gives a negative Baeyer test and is not attacked by hydrogen bromide; it is oxidized to an acid (B) ($\text{C}_{14}\text{H}_{10}\text{O}_3$) by chromic acid.

Functional Group	Oxidation Product	Gain	Loss	
RCHO	$\longrightarrow \text{RCOOH}$	1-O
RCH_2OH	$\longrightarrow \text{RCOOH}$	1-O	2-H
R_2CHOH	$\longrightarrow \text{R}_2\text{CO}$	2-H
$\text{R}_2\text{C} \begin{smallmatrix} \diagup \text{OH} \\ \diagdown \end{smallmatrix} \text{CH}_3$	$\longrightarrow \text{R}_2\text{CO}$	4-H	1-C
$\text{RCH}=\text{CH}_2$	$\longrightarrow \text{RCOOH}$	2-O	2-H	1-C
$\text{RC}\equiv\text{CH}$	$\longrightarrow \text{RCOOH}$	2-O	1-C
$\text{ArCH}_2\text{CH}_2\text{OH}$	$\longrightarrow \text{ArCOOH}$	1-O	4-H	1-C
ArCOCH_3	$\longrightarrow \text{ArCOOH}$	1-O	2-H	1-C
ArCH_3	$\longrightarrow \text{ArCOOH}$	2-O	2-H
ArCH_2CH_3	$\longrightarrow \text{ArCOOH}$	2-O	4-H	1-C
Ar_2CHCH_3	$\longrightarrow \text{Ar}_2\text{CO}$	1-O	4-H	1-C
(A) $\text{C}_{15}\text{H}_{14}\text{O}$	\longrightarrow (B) $\text{C}_{14}\text{H}_{10}\text{O}_3$	2-O	4-H	1-C

First, note that the oxidation has caused a *loss* of one carbon atom and four hydrogen atoms but a *gain* of two oxygen atoms. It

is necessary to find a functional group or several groups which will do this. It is useful in this connection to tabulate the behavior of the common functional groups on oxidation, making a note of the gain and loss in composition.

From the table on page 307 it will be noted that the oxidation of an ethyl group side chain corresponds exactly to the oxidation of A to B; in both cases there is a gain of two oxygen atoms and a loss of four hydrogen atoms and one carbon atom.

Subtracting an ethyl group from A ($C_{15}H_{14}O$) or a carboxyl group from B leaves a radical $C_{13}H_9O$. This radical is derived from some parent compound (C), $C_{13}H_{10}O$, which is stable to oxidation.

The next problem concerns the character of the functional group containing the oxygen atom. What functional groups containing only one oxygen atom are stable to oxidation? Consideration of various functional groups leads to the conclusion that the ether linkage is one possibility and that a properly substituted ketone is a second. Ketones with no hydrogen atoms on the α -carbon atoms are usually stable to oxidation. The commonest examples are diaryl ketones.

The next step consists in considering the ratio of carbon to hydrogen in the compounds A, B, and the hypothetical parent compound (C), $C_{13}H_{10}O$. These carbon and hydrogen atoms must be combined so that the resulting compound will be stable to oxidation. A completely saturated compound, C_nH_{2n+2} , would require a formula $C_{13}H_{28}$ for a thirteen-carbon-atom compound (C). Even allowing two hydrogen atoms as equivalent to the oxygen atom, it is obvious that the compound has no such ratio of carbon and hydrogen atoms. An alicyclic compound would require C_nH_{2n} or $C_{13}H_{26}$. Ordinary olefinic compounds and acetylenic compounds with enough double or triple bonds to lower the ratio of hydrogen to carbon are excluded by the stability to oxidation.

The only large class of compounds with such a low ratio of hydrogen to carbon atoms is aromatic in nature. Since benzene has six carbon atoms whereas the parent compound (C) has thirteen, the possibility of two benzene rings is suggested. This leaves one carbon atom to be accounted for.

Subtracting two phenyl radicals ($C_{12}H_{10}$) from compound C ($C_{13}H_{10}O$) leaves a residue of CO. It will be remembered that

diaryl ketones are stable to oxidation. The parent compound (C) is evidently benzophenone, $C_6H_5COC_6H_5$, and the compounds A and B are probably an ethylbenzophenone ($C_6H_5COC_6H_4CH_2CH_3$), and a benzoylbenzoic acid ($C_6H_5COC_6H_4COOH$), respectively.

Example 5. An ester, containing only carbon, hydrogen, and oxygen, possessed a saponification equivalent of 74 ± 1 .

The first step is to work out the possibilities on the assumption that the molecule contains only one ester group. In that event, the molecular weight is equal to the saponification equivalent. The type formula for an ester is $R-COO-R'$, and hence the first step is to subtract the weight of $-COO-$ from the molecular weight.

$$\text{Molecular weight} = 74 \pm 1$$

$$-COO- = 44$$

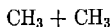
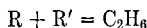
$$\text{Residue} = 30 \pm 1$$

This residue represents the combined weight of R and R'. In saturated esters¹ containing only carbon, hydrogen, and oxygen this residue must always be equal to C_nH_{2n+2} and, moreover, must always be an even number.² Thus, residual weights of 31 and 29 are impossible, and the value 30 represents the molecular weight of C_nH_{2n+2} . Mere inspection in this case shows that the hydrocarbon residue is C_2H_6 , but the logical approach is to solve for the value of n by multiplying its value by the atomic weights of the elements in the formula and setting this equal to the residual weight.

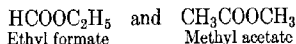
$$12n + 1(2n + 2) = 30$$

$$14n = 28 \text{ and } n = 2$$

This residue of C_2H_6 represents the sum of R and R', and it is now necessary to write the possibilities.



Hence, on the assumption that the compound was a mono-ester, two possibilities are



¹ In an olefinic ester the residue is C_nH_{2n} ; in an acetylenic ester, C_nH_{2n-2} .

² See Note 1, page 301.

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If two ester groups are present in the molecule then the molecular weight is twice the saponification equivalent. Two ester groups will contain two -COO- combinations; hence

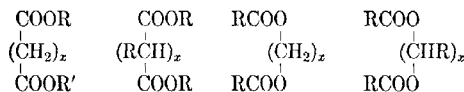
$$\begin{aligned}\text{Molecular weight} &= 2 \times 74 \pm 1 = 148 \pm 2 \\ 2\text{-COO-} &= 2 \times 44 = 88\end{aligned}$$

$$\text{Residue} = \frac{148 \pm 2}{2} = 60 \pm 2$$

The value of 60 ± 2 represents the summation of those portions of the molecule other than the two -COO- groups. Again, $\text{C}_n\text{H}_{2n+2} = 60 \pm 2$ and

$$\begin{aligned}12n + 1(2n + 2) &= 60 \pm 2 \\ 14n &= 58 \pm 2\end{aligned}$$

Since n must be an integer the only value of the right-hand side of the equation which will fulfill this requirement is 56, and, hence, $n = 4$. The residue must be C_4H_{10} and has to be divided among the various hydrocarbon radicals present in the type formulas for a compound with two ester groups. Some of the possible type formulas are



Using these type formulas for esters of a dicarboxylic acid, or a dihydroxy alcohol, possible structures may now be written in which the four carbon atoms and ten hydrogen atoms are distributed properly in each of the above formulas.

This example illustrates the use of saponification equivalents in deducing possible structures. It also shows that a saponification equivalent is not quite so useful as the neutralization equivalent of an acid. It is always desirable to have some additional data concerning either the acid or alcohol which is produced by saponification of the ester in order to reduce the number of isomeric esters which possess the required saponification equivalent.

CHAPTER XII

PROBLEMS

The following problems are designed to give the student added experience in the types of reasoning illustrated by the examples in Chapter XI. It is of the utmost importance to seek the answers by systematic procedures, and students are urged to avoid a random attack on a problem.

SET 1

In the investigation of unknown compounds the following types of behavior are observed frequently. Indicate in each instance the deductions which may be made as to the nature of the compound.

1. A Class A₂ compound was isomerized under the influence of phosphorus pentachloride in ether to a Class M compound.
2. A Class N₁ or N₂ compound, when heated with a solution of sodium hydroxide, took up the elements of sodium hydroxide and was converted to a Class S₂ compound.
3. An aldehyde reduced Tollens' but not Fehling's solution.
4. Treatment with a solution of hypochlorite transformed a Class N₁ compound into the salt of a Class A₁ compound.
5. A yellow, neutral compound containing only carbon, hydrogen, and oxygen was changed to an acid by the action of hydrogen peroxide.
6. A neutral compound reacted with phenylhydrazine to yield a product which differed from the expected phenylhydrazone by the elements of ethanol, i.e., the condensation involved the elimination not only of the elements of water but also of those of ethanol.
7. A compound containing only carbon, hydrogen, and oxygen reacted with acetyl chloride but not with phenylhydrazine. Treatment with periodic acid converted it into a compound which reacted with phenylhydrazine but not with acetyl chloride.
8. A yellow, neutral compound formed a derivative with *o*-phenylenediamine.
9. A neutral compound gave negative tests with acetyl chloride and phenylhydrazine. When heated with a concentrated solution of hydrobromic acid it yielded a derivative containing bromine.

10. An alcohol gave a positive iodoform test and a negative Lucas test.
11. A Class N_1 compound reacted with acetyl chloride but not with phenylhydrazine. Heating with mineral acids converted it to a compound which failed to react with acetyl chloride but which gave positive tests with phenylhydrazine and bromine in carbon tetrachloride.
12. A nitrogen-containing compound gave a positive nitrous acid test for secondary amines, but its derivative with benzenesulfonyl chloride was soluble in alkalies.
13. A compound, when treated with ethyl orthoformate, was found to take up the elements of ethyl ether.
14. A Class N_1 compound underwent dimerization in an ethanolic solution of sodium cyanide.
15. A Class B compound failed to react with benzenesulfonyl chloride but yielded a derivative with nitrous acid.
16. An ester had a saponification equivalent of 59 ± 1 .
17. A solid Class S_2 acid possessed a neutralization equivalent of 54 ± 1 . At temperatures above its melting point, the compound lost carbon dioxide and formed a new solid acid with a neutralization equivalent of 59 ± 1 .
18. A Class S_2 compound containing nitrogen and sulfur gave a neutralization equivalent of 142 ± 1 . Addition of barium chloride to an aqueous solution produced a precipitate insoluble in acids. Alkali caused the separation of a Class B compound whose hydrochloride had a neutralization equivalent of 130 ± 1 .
19. A Class S_1 compound containing nitrogen gave a neutralization equivalent of 73 ± 1 when titrated with standard hydrochloric acid and methyl red as the indicator. It formed a precipitate when treated with benzenesulfonyl chloride and sodium hydroxide solution.
20. A 12-g. sample of a compound, C_8H_8O , was treated with a carbon tetrachloride solution of bromine containing 60 g. of bromine. Hydrobromic acid was evolved, and a quantitative determination showed that 16.2 g. was liberated. After the reaction was complete the solution was still red, and it was found that 12 g. of bromine remained unused. Calculate the number of atoms of bromine that were introduced by substitution and, if addition also took place, the number of atoms of bromine which were added. Use $Br = 80$, $H = 1$, $C = 12$, $O = 16$.

SET 2

In solving the problems of this set and those in Sets 3 and 4, follow the steps outlined in Chapter II, using the data cited in the problems. Make the customary allowances for experimental error in boiling points and melting points.

- I (1) White crystals; m.p. $117-118^\circ$.
- (2) Elementary analysis for X, N, S—negative.
- (3) Solubility class— S_1 .
- (4) Classification tests:

$C_6H_5NHNH_2$ —negative	CH_3COCl —positive
$KMnO_4$ —positive	HIO_3 —negative
Br_2 in CCl_4 —negative	HIO_4 —positive
N.E. = 151 ± 1	

- (5) Derivative:
p-Nitrobenzyl ester, m.p. 123° .

- II (1) Colorless liquid; b.p. $259-261^\circ$.
 (2) Elementary analysis for Br—positive; for Cl, I, N, S—negative
 (3) Solubility class— N_2 .
 (4) Classification tests:
- | | |
|------------------------------|-----------------------------|
| $H_2NOH \cdot HCl$ —negative | $KMnO_4$ —negative |
| CH_3COCl —negative | Br_2 in CCl_4 —negative |
| $AgNO_3$ —negative | NaI —negative |
- Hot sodium hydroxide—clear solution which on acidification gave white crystals, m.p. 250° , containing bromine. Saponification equivalent = 229.
 (5) Derivatives.
 (a) Treatment with hydrazine gave colorless crystals; m.p. 164° .
 (b) Treatment with 3,5-dinitrobenzoic acid and sulfuric gave pale yellow crystals; m.p. 92° .

- III (1) Brown liquid; b.p. $198-200^\circ$.
 (2) Elementary analysis for X, N, S—negative.
 (3) Solubility class— A_2 .
 (4) Classification tests:
- | | |
|--------------------------|-------------------------------|
| CH_3COCl —positive | Br_2 in H_2O —precipitate |
| $C_6H_5NHNH_2$ —negative | $FeCl_3$ —violet |
| $Ce(NO_3)_4$ —positive | HIO_3 —positive |
- (5) Derivative; Treatment with chloroacetic acid gave white crystals; m.p. $102-103^\circ$.

- IV (1) Colorless liquid; b.p. $194-195^\circ$.
 (2) Elementary analysis for X, N, S—negative.
 (3) Solubility class—I.
 (4) Classification tests:
- | |
|---------------------------------|
| $H_2SO_4 \cdot SO_3$ —negative |
| $AlCl_3 + CHCl_3$ —light yellow |
- (5) Derivatives—none.
 Sp. gr. $^{20}_4 = 0.8963$ $n_D^{20} = 1.4811$

- V (1) White crystals; m.p. $187-188^\circ$.
 (2) Elementary analysis for X, N, S—negative.
 (3) Solubility class— S_1 - S_2 . Aqueous solution is acid to litmus.
 (4) Classification tests:
- | | |
|--------------------------------|-----------------------------|
| $KMnO_4$ —negative | $C_6H_5NHNH_2$ —negative |
| Br_2 in CCl_4 —negative | CH_3COCl —negative |
| Neutralization equivalent = 59 | Partition coefficient = 7.7 |

- (5) Derivative: Heating with phenylhydrazine gave white crystals, m.p. 209–210°.

- VI (1) Reddish-brown solid; m.p. 65–70°.
 (2) Elementary analysis for N—positive; for X, S—negative.
 (3) Solubility class—B. A solution of the compound in dilute hydrochloric acid was decolorized with Norite and alkali added. The compound, purified in this manner, melted at 73°.

- (4) Classification tests:

KMnO ₄ —positive	C ₆ H ₅ SO ₂ Cl + NaOH—Residue soluble in hydrochloric acid
Br ₂ in CCl ₄ —precipitate	HIO ₃ —positive
Bromine water—precipitate	Fe(OH) ₂ —negative
C ₆ H ₅ NHNH ₂ —positive	Ag ₂ O—positive

Hot sodium hydroxide decomposed the compound. After removal of a dark brown solid by filtration, the filtrate was neutralized and a light tan precipitate obtained. After recrystallization from a water-alcohol mixture, it melted with decomposition at 236–240°. It was in Class A₁(B). Acetone and sodium hydroxide gave a yellow precipitate; m.p. 134–135°.

- (5) Derivatives:

Oxime, m.p. 144°.
 Phenylhydrazone, m.p. 148°.
 Semicarbazone, m.p. 224°.

SET 3

1. A brown liquid (I) boiled at 193–195°. It contained nitrogen but gave negative tests for sulfur and the halogens. It was insoluble in water but soluble in dilute acid. It did not react with acetyl chloride or benzene-sulfonyl chloride. Treatment of a hydrochloric acid solution of the unknown compound with sodium nitrite, followed by neutralization, gave a compound (II) which melted at 83–84°. Compound II was insoluble in alkalis but dissolved in boiling concentrated sodium hydroxide solution, with the liberation of a gas (III). This gas (III) was absorbed in water, and the aqueous solution was treated with phenyl isothiocyanate; there was formed a compound (IV) with a melting point of 134–135°. Careful acidification of the above alkaline solution, followed by extraction, gave a compound (V) which melted at 125–126°.

2. A colorless liquid was found to be soluble in water and in ether. It boiled at 94–96°, and gave negative tests for the halogens, nitrogen, and sulfur. It reduced a dilute potassium permanganate solution, decolorized bromine in carbon tetrachloride, reacted with acetyl chloride, and liberated hydrogen upon treatment with sodium. It did not give iodoform when treated with sodium hypoiodite and did not react with phenylhydrazine. Treatment with 3,5-dinitrobenzoyl chloride transformed it into a compound melting at 47–48°.

3. A yellow solid (I), melting at 113–114°, contained nitrogen, but no halogens, sulfur, or metals. It was insoluble in water and alkalies but soluble in dilute acids. The acid solution of I was treated with sodium nitrite in the cold and then boiled. The product (II) of this reaction separated when the solution was cooled. It contained nitrogen and melted at 95–96°; it was insoluble in acids and sodium bicarbonate solution but soluble in sodium hydroxide solution. The products obtained by treating compounds I and II with zinc and a boiling solution of ammonium chloride readily reduced Tollens' reagent. The original compound (I) was treated with benzenesulfonyl chloride and alkali. Acidification of the resulting solution gave a compound (III) which melted at 135–138°.

4. A colorless crystalline compound (I) melted at 186–187°; it contained nitrogen, but no halogens or sulfur. It was insoluble in water and dilute acids, but was soluble in dilute sodium bicarbonate solution. It gave a neutralization equivalent of 180 ± 2 but did not react with bromine in carbon tetrachloride, dilute potassium permanganate solution, acetyl chloride, or phenylhydrazine. It was treated for some time with boiling hydrochloric acid. When this reaction mixture was cooled, a compound (II) separated which melted at 120–121°, and gave a neutralization equivalent of 121 ± 1 . The filtrate remaining after the removal of II was evaporated to dryness, and the residue (III) was purified by recrystallization. It contained nitrogen and chlorine, was rather hygroscopic, and decomposed when an attempt was made to determine its melting point. It was insoluble in ether, and its aqueous solution gave a precipitate with silver nitrate. A solution of III was treated with nitrous acid in the cold. A vigorous evolution of a gas was observed. Compound III was treated with benzenesulfonyl chloride and sodium hydroxide solution. Acidification of the resulting solution gave a new product (IV) which melted at 164–165°.

5. A colorless crystalline compound (I) melted at 162–165°, with decomposition. It gave negative tests for nitrogen, halogens, sulfur, and metals. It was soluble in water but insoluble in ether. It reacted with acetyl chloride, decolorized permanganate solution, reduced Fehling's solution and Tollens' reagent, but gave no color with Schiff's reagent. It reacted with phenylhydrazine to give a product (II) which melted, with decomposition, at 199–201°. When I was warmed with concentrated nitric acid, a vigorous reaction took place, and a compound (III) separated when the reaction mixture was cooled. This compound (III) was insoluble in water but readily soluble in alkalies; it gave a neutralization equivalent of 104 ± 1 . Compound III reacted with acetyl chloride, but not with phenylhydrazine, and melted at about 212–213°, with decomposition. If kept above its melting point for some time it was converted into a new compound (IV) which melted at 132–133°, after recrystallization. Compound IV was insoluble in water but soluble in sodium bicarbonate solution, and it gave a neutralization equivalent of 111 ± 1 . Treatment of the sodium salt of IV with *p*-bromophenacyl bromide gave a compound (V) melting at 127–128°.

The original compound (I) was optically active, having a specific rotation of $+81^\circ$, but the degradation products III, IV, and V were optically inactive.

6. A solid compound (I) gave positive tests for nitrogen, sulfur, bromine,

and potassium. It possessed no definite melting point. It was soluble in water but insoluble in ether. Addition of acid to its aqueous solution precipitated a compound (II). This product melted at 182-183° and contained nitrogen, sulfur, and bromine. It gave no precipitate with hot alcoholic silver nitrate solution and did not react with acetyl chloride, phenylhydrazine, or nitrous acid. It did not give a definite neutralization equivalent. When II was treated for a long time with boiling concentrated hydrochloric acid, it slowly dissolved. The addition of alkali to the resulting solution caused a precipitate (III) to separate. Product III contained nitrogen but no sulfur or bromine. It melted at 49-50° and reacted with acetyl chloride to give IV, which melted at 158-159°. Compound III was dissolved in hydrochloric acid, and the cold solution was treated with nitrous acid. When this solution was added to an alkaline solution of β -naphthol, an orange compound (V) which melted at 229° was formed.

The filtrate remaining, after the removal of compound III by filtration of the above alkaline reaction mixture, was evaporated to dryness. The residue was crystallized from alcohol, and a compound (VI) was obtained. This product had no definite melting point. It was soluble in water, but not in ether. Addition of hydrochloric acid to its aqueous solution gave no precipitate. It gave positive tests for sulfur, bromine, and sodium. Compound VI was melted with phosphorus pentachloride, the cold melt was extracted with benzene, and the benzene was distilled. The low-melting solid which remained was treated with ammonia. After recrystallization, the product was found to melt at 164-165°.

SET 4

1. A Class M compound containing nitrogen melted at 68°. When treated with tin and hydrochloric acid it yielded a substance which reacted with benzenesulfonyl chloride to give an alkali-soluble derivative. When the original compound was treated with zinc and a hot sodium hydroxide solution it was converted to a new substance melting at 130°.

2. A compound boiled at 166-169° and contained sulfur but no nitrogen or halogen. It was insoluble in water and dilute acids but dissolved in sodium hydroxide solutions. Its sodium derivative reacted with 2,4-dinitrochlorobenzene to give a compound melting at 118-119°. When allowed to stand in air, the original compound was slowly oxidized to a derivative melting at 60-61°.

3. A compound melted at 141-142° and contained nitrogen but no halogen or sulfur. It was insoluble in water, dilute acids, and dilute alkalis. It was unaffected by treatment with tin and hydrochloric acid. When treated for a long time with hot sodium hydroxide solution, it reacted, forming an insoluble oil (I). The oil was soluble in dilute hydrochloric acid and reacted with acetyl chloride to give a solid, melting at 111-112°. Acidification of the alkaline solution from which I was removed gave a solid melting at 120-121°, whose neutralization equivalent was 122 ± 1 .

4. A compound boiled at 159-161° and contained chlorine but no nitrogen or sulfur. It was insoluble in water, in dilute acids and alkalis, and in cold

concentrated sulfuric acid. It dissolved in fuming sulfuric acid. It gave no precipitate with hot alcoholic silver nitrate solution. Treatment with a hot solution of potassium permanganate caused the compound to dissolve slowly. The resulting solution, when acidified with sulfuric acid, gave a precipitate which melted at 138–139° and had a neutralization equivalent of 157 ± 1 .

5. A colorless liquid boiled at 188–192°. It contained only carbon, hydrogen, and oxygen. It was insoluble in water, dilute acids, and alkalis, but dissolved readily in cold concentrated sulfuric acid. It did not react with phenylhydrazine or acetyl chloride and did not decolorize a carbon tetrachloride solution of bromine. Boiling alkalis dissolved it slowly. The resulting mixture was subjected to steam distillation. The distillate contained a compound which, when pure, boiled at 129–130° and reacted with α -naphthyl isocyanate to give a derivative melting at 65–66°.

The alkaline residue, left after the steam distillation, was acidified with phosphoric acid and steam-distilled. The distillate contained an acid which gave the following Drelaux numbers: 28.6, 23.0, 16.9. The acid yielded an anilide melting at 108–109°.

6. An unknown compound was a pink solid which melted at 109–112°. Treatment with bone black and recrystallization removed the color and brought the melting point to 112–114°. The compound burned with a smoky flame and left no residue. Elementary analysis showed nitrogen to be present and sulfur and halogens to be absent.

The compound was insoluble in water and dilute alkalis but dissolved in ether and dilute acids. It reacted with benzenesulfonyl chloride to give a derivative which was soluble in alkali and melted at 101–102°. The acetyl derivative melted at 132°.

SET 5

For each of the problems in this and the following sets, give the structural formula of an organic compound which will fulfill the conditions stated and show by equations the changes which it undergoes.

1. An acid (A) containing only carbon, hydrogen, and oxygen had a neutralization equivalent of 103 ± 1 . It gave a negative test with phenylhydrazine. Treatment with sulfuric acid converted it to a new acid (B) which decolorized permanganate and bromine solutions and had a neutralization equivalent of 87 ± 1 . The original acid (A) was transformed by hypiodite to iodoform and a new acid (C) the neutralization equivalent of which was 52 ± 1 .

2. An acid had a neutralization equivalent of 97. It could not be brominated readily, even in the presence of phosphorus tribromide. Vigorous oxidation transformed it into a new acid whose neutralization equivalent was 83.

3. An optically active hydrocarbon, dissolved in cold, concentrated sulfuric acid, decolorized permanganate solutions, and readily absorbed bromine.

Oxidation converted it to an acid which contained the same number of carbon atoms as the parent substance and had a neutralization equivalent of 66.

4. A compound had a neutralization equivalent of 66. The substance was not affected by bromine in carbon tetrachloride, but heat transformed it into an acid whose neutralization equivalent was 88.

5. A base had a neutralization equivalent of 121 ± 1 . Vigorous oxidation converted it to an acid having a neutralization equivalent of 121 ± 1 .

6. An acid whose neutralization equivalent was 166 was unaffected by bromine in carbon tetrachloride but gave a positive iodoform test.

7. A compound (A) gave negative tests for nitrogen, sulfur, and halogens. It was insoluble in water but dissolved in dilute sodium hydroxide solution. Compound A gave no color with ferric chloride and did not decolorize a solution of potassium permanganate.

Treatment with concentrated hydrobromic acid converted A into two compounds. One was a Class I compound containing bromine, which gave a precipitate with sodium iodide in acetone. The other was a new acid (B) which decolorized bromine solutions and gave a color with ferric chloride. Compound B contained no halogen. The neutralization equivalents of compounds A and B were, respectively, 180 ± 2 and 137 ± 1 .

8. An optically active acid had a molecular weight of 98.

9. A compound (I) gave a red color with ferric chloride and a precipitate with 2,4-dinitrophenylhydrazine. Compound I was refluxed with 25% aqueous sodium hydroxide, and the mixture was partially distilled. The distillate contained a compound which reacted with sodium and gave a positive iodoform test. It gave a negative Lucas test.

The residue from the distillation was acidified with phosphoric acid and the mixture steam-distilled. A volatile acid was isolated. Its *p*-bromophenacyl ester had a saponification number of 257 ± 1 .

10. An acid having a neutralization equivalent of 72 was not readily attacked by bromine. It was transformed by heat into an acid whose neutralization equivalent was 100.

SET 6

1. A Class A₁ compound (I) contained nitrogen and had a neutralization equivalent of 197 ± 2 . Treatment with thionyl chloride followed by ammonium hydroxide converted I to a Class M compound (II) which reacted with an alkaline hypobromite solution to yield a Class B compound (III). Hydrolysis of compound III produced a new compound (IV), soluble in both acids and bases and having a neutralization equivalent of 186 ± 2 . Treatment of this compound with nitrous acid in the presence of sulfuric acid gave a clear solution. When cuprous cyanide was added to this solution, compound I was regenerated.

Hydrolysis of I gave an acid (V) having a neutralization equivalent of 107 ± 1 . Heat converted V into a neutral substance (VI) which could be reconverted to V by hydrolysis.

Oxidation of compound IV gave a new acid (VII) having a neutralization equivalent of 71 ± 1 .

2. An unknown (I) was insoluble in water but soluble in both dilute acid and dilute alkali. It contained nitrogen and bromine. No satisfactory neutralization equivalent could be obtained. Treatment with acetic anhydride converted it into a Class A compound (II) which gave a neutralization equivalent of 270 ± 3 . When I was treated with cold nitrous acid a gas was liberated and a compound (III) was produced which gave a neutralization equivalent of 230 ± 2 . Compounds I, II, and III when vigorously oxidized gave the same product—a bromine-containing acid whose neutralization equivalent was found to be 199 ± 2 .

3. A solid ester (I) was saponified (saponification equivalent 173 ± 2), and the alkaline aqueous solution was evaporated nearly to dryness. The distillate was pure water. The residue was acidified and distilled; a colorless oil (II) was isolated. The substance II reacted with acetyl chloride and gave a color with ferric chloride solution. The residue from the distillation yielded a solid (III) which was alkali soluble. When III was heated above its melting point it changed to IV; IV was dissolved by shaking with warm aqueous alkali, and the solution was acidified; the solid which separated was identical with III.

4. A yellow solid (I) giving a positive test for nitrogen was found to belong to Class S₂. Addition of cold alkali liberated a water-soluble, ether-soluble compound (II) which possessed an ammoniacal odor and reacted with benzenesulfonyl chloride to give a derivative insoluble in alkali. Addition of hydrochloric acid to a dilute aqueous solution of I gave a solid acid (III) which possessed a neutralization equivalent of 167 ± 2 . After it had been boiled with zinc dust and ammonium chloride solution, compound III reduced Tollens' reagent.

5. An acid giving a neutralization equivalent of 277 ± 2 could not be reduced by mild chemical reducing agents but readily absorbed three moles of hydrogen in the presence of platinum. Ozonization followed by mild oxidation gave propionic acid (1 mole), malonic acid (2 moles), and azelaic acid (1 mole).

6. An optically active compound ($C_5H_{10}O$) was found to be in solubility Class S₁-N₁. It gave negative tests with phenylhydrazine, Lucas' reagent, and hypoiodite but decolorized solutions of bromine and permanganate. It reacted with acetyl chloride. Oxidation with permanganate converted it to an acid having a neutralization equivalent of 59 ± 1 . When heated the acid lost carbon dioxide and was converted to a new acid having a neutralization equivalent of 73 ± 1 .

7. A liquid compound (I) in Class M reacted readily with sodium ethoxide to give a sodium derivative. Alkaline hydrolysis followed by careful acidification converted I into a Class A₁ compound (II). When heated, II passed into a Class N₁ compound which in turn reacted with a sodium hypochlorite solution to yield a Class A₁ compound.

8. A certain Class A₂ compound was a liquid which, when treated with tin and hydrochloric acid, gave a Class B compound. The latter was in turn completely converted into a Class N₁ compound by the action of nitrous acid. The Class N₁ compound, on treatment with phosphorus pentachloride, gave a Class I compound which yielded a Class M compound when heated with potassium cyanide.

9. A Class A_2 compound (I) was changed to a Class B compound by treatment with sodium in alcohol. Hydrolysis converted I into a Class N_1 compound. When I was treated with phosphorus pentachloride in ether it was changed to a Class M compound. Hydrolysis of the latter in the presence of alkali gave a single substance which belonged in Class S_2 .

10. A compound (I) containing carbon, hydrogen, oxygen, and nitrogen was soluble in dilute sodium hydroxide solution and in dilute hydrochloric acid but was insoluble in sodium bicarbonate solution. It reacted with an excess of acetic anhydride to give a product (II) which was insoluble in water, in dilute acids, and in dilute alkalis. Compound I decolorized bromine water; when it was dissolved in an excess of dilute hydrochloric acid and the cold solution was treated with sodium nitrite a new product (III) separated without the evolution of nitrogen.

11. A hydroxy acid had a neutralization equivalent of 64. It was not readily decomposed by heat and could not be resolved into optically active forms.

SET 7

1. When a solid, $C_9H_5O_2$ (I), was heated with a dilute solution of potassium carbonate, it was converted to the potassium salt of an acid, $C_9H_5O_3$ (II). The salt reverted to I when treated with acids. Compound I reacted with bromine in carbon tetrachloride to yield $C_9H_5O_2Br_2$ (III). When heated with a solution of sodium hydroxide, compound III gradually went into solution. Acidification of the solution precipitated a compound, $C_9H_5O_3$ (IV).

2. A compound, C_8H_5ONBr , when treated with boiling potassium hydroxide solution, gave the potassium salt of an acid, $C_8H_5O_3$, which was resolvable into *d* and *l* forms.

3. A compound, $C_{11}H_{12}O_4$ (I), reacted with hot sodium hydroxide solution to yield a salt, $C_{11}H_{13}O_5Na$ (II). Treatment of the salt with hot dilute sulfuric acid converted it to an acid, $C_8H_5O_4$ (III). Heat converted compound III to a high-melting compound, $C_{18}H_{12}O_6$ (IV).

4. A compound, $C_8H_5O_2$ (I), was changed to $C_8H_5O_2Cl$ (II) by treatment with boiling concentrated hydrochloric acid. Compound I reacted slowly with a solution of potassium hydroxide to yield $C_8H_5O_3K$ (III). This compound was converted into $C_8H_5O_3$ (IV) by treatment with an alkaline permanganate solution. Compound IV, when treated with a solution of sodium hypochlorite, was transformed into $C_8H_5O_4$ (V), an acid whose neutralization equivalent was 58 ± 1 . This acid when heated gave $C_4H_4O_3$ (VI). When the aqueous solution of II was made exactly neutral with sodium hydroxide solution the original compound (I) was slowly regenerated.

5. A liquid Class M compound had the formula $C_7H_7NO_3$.

6. A compound, $C_7H_{11}O_4Br$ (I), was insoluble in water, in dilute acids, and in dilute alkalis. When brominated it gave $C_7H_{10}O_4Br_2$. Slow hydrolysis of I by hot sulfuric acid produced $C_4H_5O_2$ (II), a neutral compound which reacted slowly with aqueous sodium hydroxide to give $C_4H_7O_3Na$.

7. A compound, $C_{16}H_{13}N$, formed salts with strong mineral acids. The salts were hydrolyzed by water.

8. A compound, $C_{14}H_{10}O$, gave $C_{12}H_{10}O_2$ when oxidized by alkaline permanganate. The original compound reacted with sodium to give $C_{14}H_9ONa$.

9. An acid of neutralization equivalent 57 was unaffected by bromine in carbon tetrachloride.

SET 8

1. A liquid, $C_9H_8O_2$ (I), decolorized a permanganate solution and also reduced Fehling's solution. When heated with an alkali cyanide, compound I dimerized. Treatment of compound I with ethyl orthoformate converted it to a new substance, $C_9H_{14}O_3$.

2. A compound, $C_9H_8O_4$ (I), was soluble in dilute sodium hydroxide solution and when treated with bromine was converted into $C_9H_6O_4Br_2$ (II). Compound I was regenerated from II by treatment of the latter with zinc dust. Compound II was converted into $C_9H_6O_4$ (III) by heating with hydrogen iodide. Compound III possessed a neutralization equivalent of 59 and lost a molecule of water when heated. The anhydride thus produced reacted with benzene in the presence of aluminum chloride to give $C_{10}H_{10}O_3$ which was soluble in alkali, reacted with phenylhydrazine, and was converted into benzoic acid by vigorous oxidation.

3. A compound, $C_{11}H_{10}N_2$, was converted by vigorous oxidation to $C_{11}H_8N_2O$.

4. A compound, $C_8H_{10}O$, decolorizes an alkaline solution of potassium permanganate but is not affected by bromine in carbon tetrachloride.

5. A compound, $C_{14}H_{12}O$, is converted by chromic acid oxidation into an acid whose neutralization equivalent is 226.

6. A neutral compound, $C_{10}H_6O_4$ (I), when heated with a sodium hydroxide solution, was converted to the salt of an acid (II) having a neutralization equivalent of 209 ± 2 . Compound I reacted with hydrogen peroxide to yield a new acid (III) having a neutralization equivalent of 111 ± 1 .

7. A compound, $C_{10}H_7O_2N$ (I), when treated with iron and hydrochloric acid was converted into $C_{10}H_9N$ (II)—a compound which was soluble in dilute hydrochloric acid. By vigorous oxidation of I and II, $C_8H_6O_6N$ and $C_8H_6O_4$, respectively, were produced. Both oxidation products were soluble in alkali.

SET 9

1. A naturally occurring compound, $C_{10}H_{16}O_2$ (I), was found to be unreactive toward acetyl chloride and phenylhydrazine. Heating with potassium hydroxide, however, brought about isomerization. The isomer (II) also failed to react with acetyl chloride and phenylhydrazine. Both isomers decolorized solutions of bromine and permanganate. Ozone converted isomer II to a compound (III) which formed a phenylhydrazone. Oxidation of compounds II or III with alkaline potassium permanganate yielded an acid, $C_8H_6O_4$ (IV).

2. A compound, $C_8H_5O_2Cl$ (I), when heated with absolute alcohol gave $C_{14}H_{20}O_4$ (II), which by oxidation with alkaline permanganate was converted into $C_8H_6O_4$. Treatment with aniline converted I into $C_{20}H_{16}ON_2$.

3. A compound, $C_8H_{14}O_3$ (I), was soluble in dilute sodium hydroxide solution and gave a red coloration with ferric chloride solution. Phenylhydrazine converted it into $C_{12}H_{14}ON_2$ (II), and refluxing with 20% hydrochloric acid transformed it (I) into $C_5H_{10}O$ (III). Compound III gave a crystalline precipitate when treated with semicarbazide but, when treated with a solution of sodium hypiodite, gave no iodoform.

4. A compound, C_9H_7N (I), was converted by catalytic reduction into $C_9H_{11}N$ (II). When compound II was treated with an excess of methyl iodide followed by silver oxide and the reaction product was heated, a compound, $C_{11}H_{13}N$ (III), was produced. This compound was converted (a) by vigorous oxidation into $C_8H_6O_4$ (IV); (b) by treatment with ozone and hydrolysis of the reaction product into $C_{10}H_{13}ON$ (V). The ozonization product yielded $C_{20}H_{25}O_2N_2$ (VI) when heated with a dilute solution of potassium cyanide. Compound VI was converted into IV by vigorous oxidation.

5. A compound, $C_{10}H_{10}O$ (I), reacted with sodium to give a derivative, $C_{10}H_9ONa$, which was completely hydrolyzed by water. Treatment of compound I with cold 80% sulfuric acid in the presence of mercuric sulfate and then with water gave $C_{10}H_{12}O_2$ (II). This compound dissolved slowly in a solution of sodium hypochlorite, and by acidification of the solution $C_8H_{10}O_3$ (III) was obtained. Boiling 48% hydrobromic acid converted compound III into $C_8H_7O_2Br$ (IV)—a compound which vigorous oxidation transformed into $C_8H_6O_4$.

6. A compound having the molecular formula $C_{14}H_{12}$ is converted by permanganate oxidation into a derivative whose molecular formula is $C_{12}H_{10}O$ and which is not affected by further treatment with permanganate.

7. An optically active compound, $C_8H_{13}N$, is converted by vigorous oxidation into an acid whose neutralization equivalent is 83.

8. A compound does not decolorize bromine water but reacts with sodium to give $C_8H_6O_3Na_2$. It has a neutralization equivalent of 152.

SET 10

1. An optically active compound, $C_9H_{11}ON$, was found to be in solubility Class M. It was hydrolyzed slowly by treatment with alcoholic alkali to give two products. One of these was the salt of a volatile acid, which decolorized a solution of potassium permanganate. The other was a Class B compound, which reacted with benzenesulfonyl chloride to give a product which was soluble in aqueous sodium hydroxide solutions.

2. A colorless, crystalline solid (I) contained nitrogen but no halogen or sulfur. It was soluble in water but insoluble in ether. Its aqueous solution was acidic and gave a neutralization equivalent of 123 ± 1 . It was treated with sodium nitrite and hydrochloric acid. A gas evolved, one-third of which was soluble in potassium hydroxide solution. The solution from the nitrous acid treatment was evaporated to dryness; only sodium chloride, sodium nitrate, and sodium nitrite were left. Compound I was heated with dilute sodium hydroxide solution; ammonia was evolved, and the solution on acidification gave off a gas. Evaporation of this solution left only inorganic salts.

3. An unknown compound containing carbon, hydrogen, oxygen, and nitrogen was insoluble in water, in dilute acids, and in dilute alkalis. It did not react with acetyl chloride or phenylhydrazine and was not easily reduced. When treated with hot aqueous alkali, the substance slowly dissolved. Distillation of this alkaline solution gave a distillate containing a compound which was salted out by means of potassium carbonate. This compound gave the iodoform test but no reaction with a hydrochloric acid solution of zinc chloride. The original alkaline solution (residue from the distillation) was acidified with sulfuric acid, and the solution was again distilled; a volatile acid was obtained in the distillate. This distillate reduced permanganate. The residual liquor from this second distillation was exactly neutralized, and a solid was obtained. This solid contained nitrogen and possessed a neutralization equivalent of 137 ± 1 .

4. An acid, $C_6H_8O_4$ (I), was converted into $C_6H_5O_2Cl_2$ (II) by phosphorus pentachloride. The chlorine derivative, when treated with benzene in the presence of anhydrous aluminum chloride, gave $C_{18}H_{16}O_2$ (III). This compound did not decolorize permanganate but readily formed a dibromide and a dioxime. The dioxime rearranged under the influence of phosphorus pentachloride to yield $C_{18}H_{18}O_2N_2$ (IV)—a compound which gave the original acid (I) when hydrolyzed.

5. A compound (I) contained carbon, hydrogen, oxygen, nitrogen, and chlorine. It was soluble in water but insoluble in ether. The aqueous solution immediately gave a precipitate with silver nitrate. When the aqueous solution of I was exactly neutralized a new compound (II) free from chlorine separated. It reacted with acetic anhydride to give an alkali-soluble, acid-insoluble compound (III) possessing a neutralization equivalent of 207 ± 2 . Compound II reacted with benzenesulfonyl chloride to give an alkali-soluble product and with nitrous acid without evolution of any gas even when heated. The product from the latter treatment still contained nitrogen and was soluble in alkalis and insoluble in acids. Vigorous oxidation of either I, II, or III gave a nitrogen-free acid, insoluble in water and in dilute hydrochloric acid, and possessing a neutralization equivalent of 82 ± 2 .

6. A compound, $C_{10}H_8O_3$ (I), decolorized alkaline permanganate and reacted with hydroxylamine. It decomposed when distilled at ordinary pressure to give $C_9H_6O_2$ (II), a compound which yielded a monosodium derivative and was readily oxidized to $C_9H_6O_4$ (III). Compound III was an acid which, when heated with soda-lime, was converted into $C_7H_6O_2$ (IV). Compound IV was decomposed by heating with dilute hydrochloric acid under pressure and yielded a Class S_1 - A_2 compound having the formula $C_6H_6O_2$.

SET 11

1. A compound (A) contained only carbon, hydrogen, and oxygen. It was insoluble in water, dilute acids, and dilute alkalis but dissolved in cold concentrated sulfuric acid. It gave negative tests with phenylhydrazine and acetyl chloride. When heated with hot aqueous sodium hydroxide it yielded an oil (B) and a volatile acid having a neutralization equivalent of 59 ± 1 .

Compound B reacted with acetyl chloride but not with phenylhydrazine. Treatment with a concentrated solution of hydrogen bromide transformed it into a bromine-containing compound (C) which gave positive tests with silver nitrate, ferric chloride, and bromine water.

Mild oxidation converted B to an acid (D) having a neutralization equivalent of 164 ± 2 .

2. A compound (I), giving positive tests for nitrogen and chlorine, was found to belong in Class A₁. A neutralization equivalent of 210 ± 2 was obtained. Compound I reacted with acetyl chloride but not with hot alcoholic silver nitrate. The acetyl derivative (II) had a neutralization equivalent of 253 ± 2 . Hot boiling alkali liberated ammonia from I, and acidification of the resulting solution precipitated a new acid (III) which had a neutralization equivalent of 115 ± 1 . Compound III contained chlorine but no nitrogen. When compound III was boiled with potassium permanganate solution, a new A₁ compound was produced which still contained chlorine and gave a neutralization equivalent of 81 ± 1 .

3. A Class N₂ compound (A) was a colorless solid which gave negative tests for nitrogen, sulfur, and the halogens. It gave positive tests with phenylhydrazine and acetyl chloride. Mild oxidation converted it to a new compound which was a yellow solid (B). The new compound reacted with phenylhydrazine to give the same derivative that was obtained from A. Vigorous oxidation of B converted it into an acid (C) which had a neutralization equivalent of 121 ± 1 .

4. A liquid (I) containing chlorine was insoluble in water, dilute hydrochloric acid, and dilute sodium hydroxide. It dissolved in cold concentrated sulfuric acid but not in phosphoric acid. It gave no precipitate with warm alcoholic silver nitrate and did not react with acetyl chloride. It gave a precipitate with phenylhydrazine but no color with Schiff's reagent. When boiled with concentrated sodium hydroxide solution, the compound (I) dissolved. The distillate from this alkaline solution gave an iodoform test. Acidification of the alkaline solution precipitated a compound (II) which contained chlorine and gave a neutralization equivalent of 156 ± 1 . Compound II was not affected by permanganate solution. After removal of compound II, a portion of the acidic filtrate was distilled, and the distillate was found to be acid to litmus. The original compound (I) gave a saponification equivalent of 113 ± 1 .

5. A liquid had a saponification equivalent of 163 ± 1 . Saponification yielded an oil, which gave a positive ferric chloride test, and an acid of neutralization equivalent 60 ± 1 .

SET 12

1. A white crystalline solid containing only carbon, hydrogen, and oxygen was found to belong in Class N₂. It gave solid derivatives with phenylhydrazine, hydroxylamine, and semicarbazide. It was heated for 15 minutes with a solution of sodium hydroxide. Acidification of the solution precipitated an acid having a neutralization equivalent of 120 ± 1 .

2. An ether-insoluble compound (I), containing nitrogen, dissolved in water, giving an alkaline solution. Titration of this solution with standard acid gave a neutralization equivalent of 37 ± 1 . Treatment of a cold solution of I with sodium nitrite and hydrochloric acid liberated a gas. The resulting solution was made distinctly alkaline, and benzoyl chloride was added. A compound (II) separated whose solubility behavior placed it in Class N₂. Compound II gave a saponification equivalent of 142 ± 1 .

3. A colorless liquid (I) gave no tests for halogen, nitrogen, sulfur, or metals. It was insoluble in water, dilute hydrochloric acid, dilute sodium hydroxide, and phosphoric acid, but soluble in cold concentrated sulfuric acid. It did not react with acetyl chloride or phenylhydrazine and was not affected by heating with sodium hydroxide. It was refluxed with dilute phosphoric acid, and an oil (II) separated when the solution was cooled. Compound II gave a precipitate with phenylhydrazine and with sodium bisulfite solution but did not react with acetyl chloride. When II was vigorously shaken with strong alkali, a compound (III) separated from the alkaline solution. This product (III) reacted with acetyl chloride but not with phenylhydrazine. Acidification of the alkaline solution gave IV, which had a neutralization equivalent of 136 ± 1 . Strong oxidation of IV gave an acid (V) with a neutralization equivalent of 82 ± 1 .

The phosphoric acid solution, from which II was separated, was distilled. The distillate was saturated with potassium carbonate, and a compound (VI) was obtained. This compound reacted with sodium and acetyl chloride and gave a yellow precipitate with sodium hypoiodite. It did not react with Lucas' reagent.

4. A solid compound was soluble in water but not in ether. It contained only carbon, hydrogen, oxygen, and nitrogen and left no residue when ignited. It gave a neutralization equivalent of 53 when titrated with a standard solution of hydrochloric acid. Treatment with acetyl chloride gave a derivative which contained nitrogen and was in solubility Class S₁. When the original compound was treated with sulfuric acid it gave off a gas which was absorbed completely by a solution of sodium hydroxide.

5. A colorless liquid (I) gave no tests for nitrogen, sulfur, or halogen. It was soluble in water and ether. It did not react with sodium, acetyl chloride, phenylhydrazine, or dilute permanganate solution. It did not decolorize bromine in carbon tetrachloride and was unaffected by boiling alkalis. When compound I was refluxed with an excess of hydrobromic acid, an oil (II) separated. This oil (II) contained bromine and readily gave a precipitate with alcoholic silver nitrate. It was insoluble in water, acids, and alkalis. After II was dried and purified it was treated with magnesium in pure ether. A reaction occurred with the liberation of a gas (III). No Grignard reagent could be detected. Treatment of II with alcoholic potassium hydroxide liberated a gas (IV) which gave a precipitate when passed into ammoniacal silver nitrate. The gas (III) did not give a precipitate with ammoniacal cuprous chloride. Both III and IV decolorized bromine water and reduced permanganate solutions. A careful examination of the action of hydrobromic acid on compound I showed that II was the only organic compound produced and that no gases were evolved during this reaction.

6. A compound (I) containing carbon, hydrogen, nitrogen, and oxygen was insoluble in dilute alkalis and acids. When heated for some time with hydrochloric acid, compound I yielded a solid acid (II) having a neutralization equivalent of 180 ± 1 . If compound I was oxidized with potassium dichromate and sulfuric acid it yielded a solid, nitrogen-containing acid (III) with a neutralization equivalent of 166 ± 1 . Compound I reacted with benzaldehyde in the presence of alkalis to give a benzal derivative.

If compound I was treated with stannous chloride and hydrogen chloride in dry ether and the resulting mixture was treated with water, a new compound (IV) whose molecular formula was C_8H_7N , resulted. A Zerewitinoff determination showed IV to possess one active hydrogen atom. IV was feebly basic and was resinsified by acids.

SET 13

1. A colorless oily liquid (I) of agreeable odor and containing only carbon, hydrogen, and oxygen reacted with phenylhydrazine but not with acetyl chloride, and it readily decolorized potassium permanganate solution. When it was treated with a concentrated sodium hydroxide solution and the reaction mixture acidified, two products were obtained: an oxygen-containing compound (II) which reacted with acetyl chloride and an acid (III) which reacted with fuming sulfuric acid and which, at 200° , lost carbon dioxide to yield an oxygen-containing compound (C_8H_6O). The latter decolorized permanganate solutions but did not react with sodium or phenylhydrazine. When I was warmed with potassium cyanide, a compound (IV) was produced which yielded an osazone and reduced alkaline copper solutions and which, on oxidation with periodic acid, was converted to the original compound (I) and to the acid (III).

2. A compound (I) in Class A_2 contained nitrogen but no sulfur or halogens. It reacted with acetyl chloride but not with phenylhydrazine. When I was refluxed with dilute acids, a new compound (II) was obtained; it was isolated by distillation from the acid solution and saturation of the distillate with potassium carbonate. Compound II did not react with acetyl chloride or Schiff's reagent but gave positive tests with phenylhydrazine and sodium bisulfite.

When compound I was warmed with phosphorus pentachloride and poured into water, a new compound (III) was obtained. Compound III still contained nitrogen but no halogen, was in Class M, and was decomposed by alkalis. By the addition of benzoyl chloride to this alkaline solution a compound (IV) was obtained whose solubility placed it in A_1 . It gave a neutralization equivalent of 220 ± 2 . When compound IV was refluxed for some time with dilute acids and distilled, two products resulted. One (V) contained no nitrogen, was in Class A_1 , and gave a neutralization equivalent of 120 ± 2 . The other proved to be identical with III. When III was treated with cold concentrated hydrochloric acid a compound (VI) was obtained which contained nitrogen and chlorine and was in Class S_2 . It liberated a gas when treated with cold sodium nitrite solution.

3. A Class S_2 compound (I) was decomposed by heat into a Class I compound (II) and a Class B compound (III). When II and III were heated together I was reformed. Both I and II gave a precipitate immediately when treated with silver nitrate. Compound III did not give a benzenesulfonamide but yielded a nitroso derivative.

4. A Class N_2 compound (I) gave positive tests for chlorine, bromine, and iodine. Alcoholic silver nitrate gave a white precipitate which was readily soluble in ammonia. Phenylhydrazine produced a precipitate, but acetyl chloride failed to react. Permanganate was slowly decolorized, as was bromine, in carbon tetrachloride. When compound I was shaken with cold dilute alkali for some time it dissolved. Acidification of the alkaline solution produced a compound (II) which gave positive tests for bromine and iodine and possessed a neutralization equivalent of 369 ± 3 . When compound I was boiled with dilute alkali and then acidified, a compound (III) precipitated which gave a test for iodine. Compound III possessed a neutralization equivalent of 306 ± 3 and reacted with both phenylhydrazine and acetyl chloride. Treatment of I or II with sodium hypochlorite and acidification yielded an A_1 compound containing iodine and having a neutralization equivalent of 146 ± 1 .

5. A Class N_2 compound (A) contained bromine but no other halogens. It did not react with hot alcoholic silver nitrate solution, acetyl chloride, phenylhydrazine, or bromine in carbon tetrachloride. It dissolved in boiling sodium hydroxide solution, but the distillate from this alkaline solution contained no organic compounds. Acidification of the alkaline solution with phosphoric acid caused the precipitation of a compound (B) which contained bromine and had a neutralization equivalent of 200 ± 2 . Steam distillation of the acid solution gave a distillate which was repeatedly extracted with chloroform. Removal of the chloroform left a colorless liquid (C) which was purified by distillation. Compound C contained no bromine and was in solubility Class S_1-A_1 . It had a neutralization equivalent of 102 ± 1 . After removal of C the solution remaining in the steam-distillation flask was made distinctly alkaline, benzoyl chloride added, and the mixture shaken vigorously. A new compound (D) separated from the alkaline solution. Compound D contained no bromine and was in Class N_2 . It had a saponification number of 135 ± 1 .

SET 14

1. A compound (I) which contained only carbon, hydrogen, and oxygen had a neutralization equivalent of 179 ± 1 . When it was heated with aqueous sodium hydroxide and the reaction mixture was acidified with sulfuric acid, a solid (II) separated which was soluble in alkalis and had a neutralization equivalent of 138 ± 1 . Compound II decolorized bromine water and gave a color with ferric chloride. Distillation of the filtrate from II yielded an acid (III) with a neutralization equivalent of 60 ± 1 .

2. A compound (I) containing nitrogen was insoluble in water and dilute alkalies but soluble in dilute hydrochloric acid. Treatment with benzenesulfonyl chloride and alkali gave a clear solution. Acidification of this solu-

tion produced a precipitate which dissolved in an excess of the acid. The original compound did not react with phenylhydrazine but was decomposed by boiling with hot sodium hydroxide solution. An oil (II) was separated from the alkaline solution (III). The oil still contained nitrogen and was soluble in dilute hydrochloric acid. Compound II gave a precipitate with bromine water and reacted with acetyl chloride and sodium. When compound II was treated with benzenesulfonyl chloride and alkali an oil remained which proved to be soluble in hydrochloric acid. Compound II was dissolved in ether, the solution saturated with hydrogen chloride, and a solid compound (IV) separated. Compound IV was soluble in water and gave a neutralization equivalent of 187 ± 1 .

Acidification of the above alkaline solution (III) produced a precipitate (V) which dissolved in an excess of acid. Addition of sodium nitrite to the ice-cold acid solution of V gave a clear solution without the evolution of nitrogen. Addition of this solution to a solution of sodium β -naphthoxide gave a red solution. Compound V gave a neutralization equivalent of 137 ± 1 .

3. A solid (I) gave tests for nitrogen, sulfur, and bromine. It was insoluble in ether but dissolved in water to give an acid solution. It gave a neutralization equivalent of 221 ± 2 . Addition of cold alkali caused an oil (II) to separate, which contained bromine and nitrogen but no sulfur. Compound II reacted with benzenesulfonyl chloride and alkali to give a clear solution from which acid precipitated III, which contained bromine, nitrogen, and sulfur. Compound II did not give a precipitate with silver nitrate but decolorized both bromine water and dilute permanganate solution. Treatment of I with nitrous acid in the cold gave a clear solution without the evolution of any gas. This solution was poured into cuprous cyanide solution, and a compound (IV) separated. Compound IV still contained bromine and nitrogen but was insoluble in dilute acids and alkalies. When IV was boiled with dilute sulfuric acid for some time, it was converted to V. This compound no longer contained nitrogen but did contain bromine. It (V) was insoluble in water and dilute hydrochloric acid but soluble in sodium bicarbonate. A neutralization equivalent of 200 ± 2 was obtained. Compound V did not react with silver nitrate or permanganate.

4. A pale yellow crystalline compound (I), giving tests for nitrogen and bromine, was insoluble in water, dilute acids, and alkalies. It did not react with phenylhydrazine, acetyl chloride, or cold dilute permanganate. Cold alcoholic silver nitrate did not react, but after boiling for some time a precipitate of silver bromide formed. When compound I was heated with zinc and ammonium chloride solution and the mixture filtered it was found that the filtrate reduced Tollens' reagent. Vigorous oxidation produced a new compound (II) which still contained bromine and nitrogen and was insoluble in hydrochloric acid but soluble in sodium bicarbonate solution. It had a neutralization equivalent of 145 ± 1 .

Treatment of compound I with tin and hydrochloric acid followed by alkali gave a new compound III which contained nitrogen and bromine and was soluble in dilute hydrochloric acid. Compound III gave a precipitate with bromine water, reacted with acetyl chloride, and gave a clear solution when treated with benzenesulfonyl chloride and alkali. Vigorous oxidation

of III produced a white crystalline Class A₁ compound (IV). Compound IV gave no tests for bromine or nitrogen and had a neutralization equivalent of 82 ± 1 .

5. A light yellow solid (I) contained chlorine and was in Class N₂. It did not react with hot alcoholic silver nitrate, acetyl chloride, or bromine in carbon tetrachloride. It gave a precipitate with phenylhydrazine. Compound I was not attacked by cold alkalis, but when it was refluxed for some time with concentrated sodium hydroxide a clear solution resulted. The distillate from this alkaline solution contained no organic compounds. Acidification of the alkaline solution with phosphoric acid gave a precipitate (II), which was removed by filtration. No organic compounds could be obtained from the filtrate by distillation or evaporation to dryness.

Compound II contained chlorine, gave a neutralization equivalent of 297 ± 2 , and reacted with acetic anhydride to produce a compound (III) which had a neutralization equivalent of 340 ± 3 . Compound III did not react with bromine water, bromine in carbon tetrachloride, or phenylhydrazine.

Vigorous oxidation of I with alkaline permanganate gave a very good yield of a product, IV, which contained chlorine and possessed a neutralization equivalent of 156 ± 1 . No other oxidation product could be found.

Vigorous oxidation of II or III with potassium dichromate and sulfuric acid also produced IV but in very poor yield.

SET 15

1. An acid (I) was found to have a neutralization equivalent of 151 ± 2 . Treatment in the cold with acetyl chloride converted it to a new acid (II) which had a neutralization equivalent of 193 ± 2 . Gentle oxidation of I with cold potassium permanganate solution transformed it to an acid (III) having a neutralization equivalent of 149 ± 2 . Compound III yielded a derivative with phenylhydrazine. Vigorous oxidation of I, II, or III yielded an acid (IV) having a neutralization equivalent of 122 ± 1 .

2. A compound (I) had a neutralization equivalent of 223. Vigorous oxidation converted it to a new acid (II) having a neutralization equivalent of 167. Treatment of I with zinc and hydrochloric acid gave an acid (III) with a neutralization equivalent of 179. Compounds I, II, and III were found to contain nitrogen.

3. A sulfur-containing compound was soluble in strong alkalis but not in sodium bicarbonate solutions. Vigorous oxidation gave a sulfur-containing acid having a neutralization equivalent of 102 ± 1 . When this compound was treated with superheated steam a sulfur-free acid was formed.

4. A Class B compound was found to be very soluble in hot water. When it was treated with hot alkali a brown oil separated. When subjected to the Hinsberg test the oil gave a product which was insoluble in dilute acids and dilute alkalis. The alkaline solution remaining after removal of the oil was acidified. Distillation gave a volatile acid having a neutralization equivalent of 60 ± 1 .

5. A compound (I) containing chlorine gave positive tests with alcoholic silver nitrate, sodium hypiodite solution, and acetyl chloride. Hydrolysis with sodium bicarbonate yielded a chlorine-free compound (II) which gave a positive iodoform test and was oxidized by periodic acid to a single compound (III). Compound III also gave a positive iodoform test.

6. A compound (A), containing only carbon, hydrogen, and oxygen, was found to react with acetyl chloride but not with phenylhydrazine. Oxidation with periodic acid converted it to a new compound (B), which reduced Tollens' but not Fehling's reagent. Treatment of B with potassium cyanide in aqueous ethanol converted it to a new compound (C), which gave positive tests with acetyl chloride and phenylhydrazine. Oxidation of C with Fehling's solution or nitric acid converted it to a yellow compound (D) which yielded a derivative with *o*-phenylenediamine. When D was treated with hydrogen peroxide it yielded an acid (E) having a neutralization equivalent of 135 ± 1 . Catalytic hydrogenation of C or D produced the original compound (A).

7. A solid, neutral substance (A) contained nitrogen. It was recovered from attempted hydrolyses with dilute acids and bases. It gave negative tests with acetyl chloride, bromine in carbon tetrachloride, sodium hypiodite solution, and Tollens' reagent. It reacted slowly with dinitrophenylhydrazine and, after treatment with zinc and ammonium chloride, it reduced Tollens' reagent.

When A was treated with hydroxylamine hydrochloride in pyridine, it was slowly converted to a new compound B. The substance B was treated with phosphorus pentachloride, which changed it to C. Boiling with acid converted C to D, a nitrogen-containing acid of neutralization equivalent 168 ± 2 , and the salt of a base E. The hydrochloride of E had a neutralization equivalent (by titration with alkali) of 195 ± 2 .

The acid D was treated with thionyl chloride, and the product was added to aqueous ammonia. The neutral substance so obtained was treated with bromine and sodium hydroxide solution. The product (F) was an acid-soluble substance which, after treatment with hydrochloric acid and sodium nitrite, gave a color with β -naphthol. Treatment of F with tin and hydrochloric acid produced G, a substance readily attacked by oxidizing agents. The compound G did not give a crystalline derivative when treated with benzil.

The base E, obtained in the reaction with phosphorus pentachloride, reacted with sodium nitrite and dilute sulfuric acid. The resulting solution gave a color with β -naphthol. Boiling the aqueous solution produced a nitrogen-free substance H, which dissolved in aqueous alkali but not in aqueous sodium bicarbonate. Oxidation of either E or H produced an acid (neutralization equivalent, 83) which was readily converted to an anhydride. The substance H did not undergo coupling with benzenediazonium solutions.

APPENDIX

Apparatus

1. Individual Desk Equipment.

It has been found convenient to assign each student a standard organic laboratory desk equipped with the usual apparatus required for the first year's work in organic preparations. This is supplemented by a special kit containing apparatus for carrying out classification tests and preparation of derivatives on a small scale.

Suggested Supplementary Kit

- 12 Test tubes, Pyrex, 16 x 125 mm.
- 12 Test tubes, Pyrex, 13 x 100 mm.
- 12 Test tubes, soft glass, 10 x 75 mm.
- 1 Pipet, graduated 1 ml.
- 1 Pipet, graduated 10 ml.
- 5 Medicine droppers
- 2 Beakers, Pyrex, 50 ml.
- 1 Hirsch funnel No. 000
- 1 Hirsch funnel No. 0000
- 1 Büchner funnel, 50 mm.
- 1 Filter flask, 50 ml.
- 1 Stainless-steel spatula, small
- 1 Porcelain crucible and cover, No. 00
- 1 Hand scale balance with two 0.1-g., one 0.2-g., one 0.5-g. weights
- 1 Desiccator, small
- 1 Flask, distilling, 25 ml.
- 1 Flask, distilling, 10 ml.
- 2 Side-arm test tubes, Pyrex, 15 x 125 mm.
- 2 Side-arm test tubes, Pyrex, 20 x 150 mm.

2. General Laboratory Equipment.

- Drying ovens, electric or steam
- Balances, triple-beam-type
- Maquenne block, gas-heated

3. Special Laboratory Equipment.

The following apparatus should be kept in a separate room away from all corrosive fumes.

- Quantitative analytical balances and analytical weights
- Refractometer, Abbe type such as Valentine (Industro-Scientific Co. Philadelphia, Pa., or Bausch and Lomb, Rochester, N. Y.)

Fisher-Davidson gravitometer
 Polarimeter
 Dennis melting-point apparatus

4. Items obtained by temporary loan from instructor or store room.

Platinum wire, about 2 in. long, No. 20, sealed into a glass rod
 Platinum foil, about 1 in. square, sealed into a glass rod
 Polarimeter tubes, one 1 dm., one 2 dm. long

Chemicals for Laboratory Shelf

Organic Compounds

The following chemicals are useful for carrying out solubility and classification tests and for preparing some (but not all) derivatives. It has been found convenient to provide a set of bottles of about 100-ml. capacity, using wide-mouth g.s. bottles for solids and tincture-mouth g.s. bottles for liquids. Larger bottles (about 500 ml.) should be used for common solvents such as acetone, benzene, chloroform, carbon tetrachloride, dioxane, ether, ligroin (70-90°), and toluene. For a class of twenty students, about 20 to 50 g. of the organic compounds may be placed in these shelf bottles, although, for economy in purchasing chemicals, they may be bought in units of 50, 100, or 500 g. The actual amounts needed per student will naturally vary with the nature of the unknowns, the intelligence with which the classification tests are selected, and the manipulative skill of the student.

Acetanilide	Benzyl chloride
Acetic anhydride	Benzyl isothiourethane hydrochloride
Acetone	α -Toluenesulfonyl chloride
Acetophenone	Biphenyl
Allyl alcohol	<i>p</i> -Bromoaniline
Allyl chloride	Bromobenzene
<i>p</i> -Aminophenol	<i>p</i> -Bromobenzenesulfonyl chloride
Ammonium benzoate	<i>p</i> -Bromobenzyl bromide
Amylene	<i>p</i> -Bromobenzyl chloride
Aniline	<i>p</i> -Bromophenacyl bromide
Aniline hydrochloride	<i>p</i> -Bromophenylhydrazine
Anisole	<i>p</i> -Bromophenyl isocyanate
Azoxybenzene	<i>n</i> -Butyl alcohol
Benzaldehyde	<i>sec</i> -Butyl alcohol
Benzamide	<i>t</i> -Butyl alcohol
Benzene	<i>n</i> -Butyl bromide
Benzidine	<i>sec</i> -Butyl bromide
Benzoic acid	<i>t</i> -Butyl bromide
Benzonitrile	<i>n</i> -Butyl ether
Benzophenone	<i>n</i> -Butyraldehyde
Benzyl alcohol	Camphor
Benzylamine	Carbon disulfide

Carbon tetrachloride	<i>p</i> -Iodophenacyl bromide
Chloroacetic acid	Isoamyl alcohol
α -Chloroacetophenone	Isopropyl alcohol
Chlorobenzene	Lactic acid (85%)
<i>p</i> -Chlorobenzhydrazide	Lactose
Chloroform	Lauryl alcohol
<i>p</i> -Chloronitrobenzene	Ligroin (70–90°)
<i>p</i> -Chlorophenacyl bromide	Maleic anhydride
Cinnamic acid	Maltose
Cyclohexane	Mercaptoacetic acid (thioglycolic acid)
<i>p,p'</i> -Diaminodiphenylmethane	Mesitylene
<i>p</i> -Dibromobenzene	Methone
Diethylamine	Methyl alcohol
Diethylene glycol	Methylaniline
<i>p</i> -Dimethylaminobenzaldehyde	Methyl iodide
Dimethylaniline	Methyl <i>p</i> -toluenesulfonate
2,4-Dinitroaniline	Naphthalene
<i>m</i> -Dinitrobenzene	β -Naphthol
3,5-Dinitrobenzoic acid	α -Naphthoquinone
3,5-Dinitrobenzoyl chloride	β -Naphthylhydrazine
2,4-Dinitrochlorobenzene	α -Naphthalenesulfonyl chloride
2,4-Dinitrophenylhydrazine	<i>m</i> -Nitroaniline
3,5-Dinitrophenyl isocyanate	<i>p</i> -Nitroaniline
Dioxane	<i>p</i> -Nitrobenzazide
Diphenylcarbamyl chloride	Nitrobenzene
Ethyl acetate	<i>m</i> -Nitrobenzenesulfonyl chloride
Ethyl acetoacetate	<i>m</i> -Nitrobenzhydrazide
Ethyl benzoate	<i>p</i> -Nitrobenzoic acid
Ethyl bromide	<i>p</i> -Nitrobenzoyl chloride
Ethylene bromide	<i>p</i> -Nitrobenzyl chloride
Ethylene glycol	<i>p</i> -Nitrophenol
Formalin	<i>p</i> -Nitrophenylhydrazine
Formic acid	<i>p</i> -Nitrophenyl isocyanate
Fructose	3-Nitrophthalic anhydride
Galactose	Oxalic acid
Gardinol (sodium lauryl sulfate)	Pentane
Glucose	2-Pentanol
Glycerol	2-Pentene
<i>n</i> -Heptaldehyde	Petroleum ether (40–60°)
<i>n</i> -Heptyl alcohol	Phenacyl bromide
Hexane	Phenol
Hydrazine hydrate	<i>o</i> -Phenylenediamine
Hydrazine sulfate	α -Phenylethylamine
Hydriodic acid (57%)	Phenylhydrazine
Hydroquinone	Phenylhydrazine hydrochloride
<i>p</i> -Hydroxybenzoic acid	<i>p</i> -Phenylphenacyl bromide
Hydroxylamine hydrochloride	Phenylsemicarbazide
Iodic acid reagent	

Phloroglucinol	Tartaric acid
Phthalic anhydride	Tetrachlorophthalic anhydride
Phthalimide	Thiourea
Picric acid	Toluene (anhyd.)
Piperazine	<i>p</i> -Toluenesulfonic acid
<i>n</i> -Propyl alcohol	<i>p</i> -Toluidine
Pseudosaccharine chloride	<i>p</i> -Tolylsemicarbazide
Pyridine (over potassium hydroxide)	Triethanolamine
Resorcinol	Triethylamine
Salicylaldehyde	1,3,5-Trinitrobenzene
Salicylic acid	Trityl chloride
Semicarbazide hydrochloride	Urea
Sucrose	Xanthinol
Sulfanilic acid	Xylene

Inorganic Compounds

The amounts suggested are suitable for a class of twenty students, although some of the bottles of the more commonly used reagents may have to be refilled several times in a semester.

Ammonium carbonate	100 g.	Potassium permanganate	200 g.
Ammonium chloride	100 g.	Potassium persulfate	25 g.
Calcium chloride (anhyd.)	1 kg.	Potassium thiocyanate	100 g.
Chromium trioxide	100 g.	Sodium acetate (anhyd.)	200 g.
Copper sulfate (anhyd.)	50 g.	Sodium acetate (cryst.)	100 g.
Ferrous ammonium sulfate	100 g.	Sodium bicarbonate	1 kg.
Hydriodic acid (57%)	100 g.	Sodium bisulfate (anhyd.)	100 g.
Iodine (resublimed)	100 g.	Sodium bisulfite	1 kg.
Iron powder	100 g.	Sodium carbonate (anhyd.)	1 kg.
Lead acetate	150 g.	Sodium chloride	1 kg.
Lead peroxide	100 g.	Sodium dichromate	1 kg.
Magnesium sulfate (anhyd.)	1 kg.	Sodium hydroxide (pellets)	1 kg.
Magnesium turnings	100 g.	Sodium, metal (under toluene)	50 g.
Mercuric bromide	10 g.	Sodium nitrate	100 g.
Mercuric chloride	100 g.	Sodium nitrite	200 g.
Mercuric iodide	10 g.	Sodium nitroprusside	5 g.
Mercuric nitrate	100 g.	Sodium sulfate (anhyd.)	1 kg.
Mercuric oxide	50 g.	Sodium sulfide (cryst.)	50 g.
Mercuric sulfate	50 g.	Sodium thiosulfate (cryst.)	100 g.
Phosphoric acid (85%)	1 kg.	Stannous chloride	100 g.
Potassium bromide	100 g.	Tin (granular)	200 g.
Potassium carbonate (anhyd.)	1 kg.	Zinc (dust)	200 g.
Potassium cyanide	100 g.	Zinc chloride (anhyd.)	100 g.
Potassium hydroxide (pellets)	1 kg.		
Potassium iodide	100 g.		

Miscellaneous Compounds, Reagents, and Solutions

It is convenient to make up 500-1000 ml. of the solutions and keep them on a side shelf and table in the laboratory. Directions for their preparation are given in Chapter VII and in textbooks on qualitative and quantitative inorganic chemistry.

Ammonium hydroxide solution (2%)
Benedict's reagent
Bogen's indicator solution
Bromine in carbon tetrachloride solution (5%)
Bromine-water (saturated)
Calcium chloride solution (saturated)
Ceric nitrate reagent
Chlorine water (fresh)
Congo red paper
Cotton
Dareo
2,4-Dinitrophenylhydrazine reagent
Fehling's solution No. 1
Fehling's solution No. 2
Ferric chloride solution (1%)
Ferrous ammonium sulfate solution (50 g./l.)
Ferrox test paper
Fuchsin aldehyde reagent
Glass wool
Grammercy indicator solution
Hydrochloric acid, standard solution (0.25 *N*) (5 gal. carboy)
Hydrochloric acid-zinc chloride solution (Lucas reagent)
Hydrogen peroxide (3%)
Hydroxylamine hydrochloride reagent
Iodic acid reagent
Iodine-potassium iodide solution
Kieselguhr
Lead acetate solution (1%)
Magnesium-potassium carbonate mixture
Mercuric chloride (10% in absolute ethanol)
Mineral oil (Stanolind)
Nickel chloride-carbon disulfide reagent
Nickel chloride-5-nitrosalicylaldehyde reagent
Nitric acid, dilute (5%)
Norite
Periodic acid reagent
Phenolphthalein indicator solution (1% in 95% ethanol)
Phosphoric acid solution (20%)
Potassium hydrogen fluoride solution (20%)
Potassium hydroxide alcoholic (10%)
Potassium permanganate solution (1%)
Silver nitrate, alcoholic (2%)
Silver nitrate, aqueous (5%)

Sodium bicarbonate solution (5%)
 Sodium bisulfite, aqueous-alcoholic
 Sodium carbonate solution (10%)
 Sodium ethoxide, alcoholic (1%)
 Sodium hydroxide, standard solution (0.1 *N*) (5 gal. carboy)
 Sodium hydroxide solution (20%)
 Sodium iodide in acetone
 Starch-iodide test paper
 Sulfuric acid, dilute (10%)
 Thymol blue indicator solution (0.2% in 95% ethanol)
 Zirconium-alizarin test paper

Chemicals Kept under a Hood

Acetyl chloride	Phenyl isocyanate
Aluminum chloride (anhyd.)	Phenyl isothiocyanate
Ammonium polysulfide	Phosphorus oxychloride
Benzenesulfonyl chloride	Phosphorus pentachloride
Benzoyl chloride	Phosphorus trichloride
Bromine	Phthalyl chloride
Chlorosulfonic acid	Sulfuric acid (fuming)
Hydrogen sulfide water	Thionyl chloride
α -Naphthyl isocyanate	<i>p</i> -Toluenesulfonyl chloride
α -Naphthyl isothiocyanate	<i>p</i> -Tolyl isocyanate
Nitric acid (fuming)	

Student Desk Reagents

Reagent Grade chemicals in 250-ml. g.s. bottles
 Acetic acid, glacial
 Ammonium hydroxide, sp. gr. 0.90, 28% NH_3
 Hydrochloric acid, concentrated sp. gr. 1.19, 37% HCl
 Hydrochloric acid solution, 10%
 Nitric acid, concentrated, sp. gr. 1.42, 70% HNO_3
 Sodium hydroxide solution, 10%
 Sulfuric acid, concentrated, sp. gr. 1.84, 95% H_2SO_4

Special Chemicals Obtained from Stock Room

Ethanol 95%	Ethyl ether, absolute
Ethanol, absolute	Chloroplatinic acid

Unknowns

These compounds should be carefully selected for purity and typical examples may be chosen from the tables in Chapter IX but not necessarily limited to the compounds listed there. About 5 to 10 g. of a solid and 10 to 15 ml. of a liquid will be sufficient. Mixtures should also contain 5 to 10 g. of a solid and 10 to 15 ml. of a liquid plus larger amounts of a suitable solvent.

As the experience and technic of the student improve toward the end of the semester, much smaller amounts of unknowns may be given and the solubility, classification tests, and preparation of derivatives carried out on much smaller scale (about one-tenth the amounts specified in the experiments and procedures).

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